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## LIST OF ERRATA

*Discovered since the publication of the book.*

- Page 2, lines 7 and 16 from top, for 0·0108 read 0·108.
- Page 30, line 8 from top, omit the words "divided by" and read "the number of CC used must be taken as the divisor for the number which should have been used had the acid," &c.
- Page 73, in the table for Organic Acids, Citric Acid (cryst.), read  $C_4H_5O_4 + HO$ , atomic weight 67 if crystallized from hot solution ;  $C_{12}H_5O_{11} + 3H_2O + 2HO$ , atomic weight 69 if crystallized from cold solution.
- Page 79, line 2 from top, read 0·00563 instead of 0·0563.
- Page 131, in the list of factors for converting metallic iron and the double iron salt into zinc and its compounds, the following corrections are necessary—0·05809 instead of 0·5809, 0·0724 instead of 0·724, 0·0829 instead of 0·3829, and 0·1034 instead of 0·1039.
- Page 134, line 19 from top, read 1·00636 instead of 1·0363.
- Page 137, line 8 from top, read 0·778 instead of 0·178.
- Page 159, line 2 from top, read grn. instead of Gm.
- Page 184, line 11 from bottom, read delicacy instead of delivery.
- Page 202, line 4 from bottom, read 50·422 instead of 50·218 ; bottom line, read 504·2 instead of 502·2.
- Page 260, line 13 from bottom, read 0·172 Gm. and 1·72 grn. instead of 0·122 Gm. and 1·22 grn.





A  
SYSTEMATIC HANDBOOK  
OF  
VOLUMETRIC ANALYSIS  
OR,  
THE QUANTITATIVE ESTIMATION OF CHEMICAL  
SUBSTANCES BY MEASURE

ADAPTED TO THE REQUIREMENTS  
OF PURE CHEMICAL RESEARCH, PATHOLOGICAL CHEMISTRY,  
PHARMACY, METALLURGY, MANUFACTURING CHEMISTRY, PHOTOGRAPHY, ETC.  
AND FOR THE VALUATION OF SUBSTANCES USED IN  
COMMERCE, AGRICULTURE, AND THE ARTS.

BY  
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LONDON:  
JOHN CHURCHILL & SONS, NEW BURLINGTON STREET.  
1863.

~~100. 6. 83.~~  
193. 6. 29.



## PREFACE.

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THE rapid strides in all branches of industrial science and art during the last ten or fifteen years have, in a great measure, been aided, if not instigated, by chemical knowledge; and not the least important part of this knowledge relates to chemical analysis, or the determination of the nature, constitution, or economic value of various agents and products used in, or resulting from, manufacturing processes.

The same remark applies, also, to certain branches of the fine arts, together with medicine, pharmacy, agriculture, and general commerce, so that practical chemistry has become a thing of general need in technology. Under these circumstances, therefore, it is not surprising that the energies of scientific men have been taxed to devise new and rapid methods of chemical analysis to meet the wants of these high-pressure times; and such a branch has been developed in volumetric analysis, by

which a large amount of time, labour, and therefore cost has been saved, as compared with the older methods of research.

Some idea of the extent to which this system has grown, may be obtained by a glance at the following pages, which are devoted, not to a history of all the processes that have been devised and advocated, but exclusively to those which have been well tried and found worthy of confidence, for, like all new branches of science, volumetric analysis has had an abundant crop of weeds and rubbish, together with, here and there, sound fruit.

It is not to the labours of English chemists, however, that this department of practical chemistry is indebted for its main growth, but to those of Germany and France, who appear to have recognized more readily than ourselves the value of the system.

In proof of this we have only to remember the names of Gay Lussac, Descroillez, Liebig, Bunsen, and Mohr, who have been the founders of it; nevertheless, the services rendered to it by our own countrymen—Faraday, Penny, Ure, Griffin, and others, are by no means contemptible.

Up to the present time, with the exception of a small and somewhat exclusive book,\* written by Mr. Scott, of

\* Longmans.

the Trinity Office, Dublin, there has been no English text-book on the subject; the want of this has been felt, and often expressed. I trust I shall not be thought presumptuous in hoping that this treatise will supply that want. The experiments, made in connection with the various processes for the purpose of testing their accuracy, have extended over several years, and amounted in number to many thousands; the book is, therefore, based on the right foundation, granting only (and this is of the utmost importance) that the foundation be rightly laid. Very little will be found in it in the way of originality or personal discovery, for I hold to the doctrine advanced by the wisest of men, that "in the multitude of counsellors there is safety," and consequently have adhered mainly to those processes which have received the approval of general experience. Nevertheless, I trust, that whatever is new in system or arrangement, may find a generous reception.

The necessities of the present day require that analytical investigations should be directed into many channels hitherto open only to the purely scientific chemist, but I doubt not that the introduction of the simpler and more expeditious methods of determination comprised in volumetric analysis, will, in some measure, put it within the power of the educated pharmaceutical chemist or chemical manufacturer, to exercise this power, either for his own or

others' benefit, and thus leave the man of science to follow the higher paths of that vast territory yet open to genius.

The student and the uninitiated must not, however, imagine that the possession of this or any other book of its class will put him into a royal road to chemical analysis. The only real method of progress is that which is gained by honest and truthful practice, beside which, to make the best and most reliable use of the system, the operator must possess a good knowledge of the laws of chemical combination and decomposition, so as to know where he may apply any of the processes here given with security. Had the book been written with a view to provide this necessary knowledge, it must have been a work of much larger dimensions, and would then probably not have been so useful as many books already in existence, devoted to general chemistry and the principles of analysis; among which, the student who desires this preliminary knowledge, cannot do better than consult Fowne's "Manual of Chemistry;" Abel and Bloxam's "Handbook of Chemistry;" Miller's "Elements of Chemistry;" and the latest editions of Fresenius' "Qualitative and Quantitative Analysis."

The main feature of volumetry is not so much analysis, in the proper sense of the term, as the quantitative determination of one principal constituent of a substance,

and in many cases of this kind the accuracy obtained by an ordinarily careful operator, such as in alkalimetry, for example, leaves nothing to be desired ; while under other circumstances, such as the estimation of one particular metal in a solution containing other metallic compounds, the operation may require the exercise of much more judgment and skill. I have endeavoured to provide, as far as possible, for these difficulties, by special explanations.

The matter contained in Part V is an attempt to make the volumetric system of examination complete and exhaustive, so far as certain substances are concerned, and though not in every case such as I should, *by preference*, use in my own laboratory, yet I believe, will be found worthy of confidence. The value of this department consists, mainly, in the fact that the determinations can mostly be made with simple and inexpensive apparatus, and are within the reach of any well-informed medical man or pharmaceutical chemist ; the latter of whom, in provincial districts, ought to be able to estimate the value of a sample of alkali, bleaching powder, or manganese, or determine the principal constituents of water, urine, manures, or soils, when called upon to do so.

The section on the analysis of urine, includes the estimation of almost every constituent likely to be required, and though written as concisely as possible, I hope it will be found suitable to the wants of the medical student.



No pains have been spared, either on my own or the printer's part, to render the book thoroughly accurate; but in a book of this character, containing so many figures and technical expressions, it is a thing of no small difficulty; especially, if it be considered, that the only time at my disposal for either writing or revising the book, has been at the beginning or close of a full day's work; nevertheless, I trust that whatever errors may yet be found will be of minor importance.

FRANCIS SUTTON.

NORWICH,

*January, 1863.*

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**Names of Elementary Substances of Ordinary Occurrence, with their  
Symbols and Atomic Weights, as Given by the Latest and Best  
Authorities.**

NAME.	SYMBOL.	ATOMIC WEIGHT.
Aluminium .....	Al	13.75
Antimony .....	Sb	122
Arsenic .....	As	75
Barium .....	Ba	68.5
Bismuth .....	Bi	208
Boron .....	B	11
Bromine .....	Br	80
Cadmium .....	Cd	56
Calcium .....	Ca	20
Carbon .....	C	6
Chlorine .....	Cl	35.46
Chromium .....	Cr	26.24
Cobalt .....	Co	29.49
Copper .....	Cu	31.7
Fluorine .....	F	19
Gold .....	Au	196.67
Hydrogen .....	H	1
Iodine .....	I	127
Iron .....	Fe	28
Lead .....	Pb	103.57
Lithium .....	Li	6.5
Magnesium .....	Mg	12
Manganese .....	Mn	27.57
Mercury .....	Hg	100
Molybdenum .....	Mo	46
Nickel .....	Ni	29.5
Nitrogen .....	N	14
Oxygen .....	O	8
Palladium .....	Pd	53.24
Phosphorus .....	P	31
Platinum .....	Pt	98.94
Potassium .....	K	37.11
Silicium .....	Si	14
Silver .....	Ag	107.97
Sodium .....	Na	23
Strontium .....	Sr	43.75
Sulphur .....	S	16
Tin .....	Sn	59
Uranium .....	Ur	59.4
Zinc .....	Zn	32.53

### Abbreviations and Explanations.

The normal temperature for the preparation and use of standard solutions is 62° Fahr. (= 16·5° C.)

CC denotes cubic centimeter.

Gm. „ gramme=15·43235 grains.

grn. „ grain.

dm. „ decem=10 fluid grains.

1 Litre=1000 CC.

1 CC=1 Gm. distilled water at 62° Fahr.

1 dm.=10 grn. „ „ „

Distilled water is to be used in all the processes, unless otherwise expressed.

Normal Solutions are those which contain 1 atom or equivalent of substance, weighed in grammes per litre or in grains per 100 dm.

Decinormal Solutions are those which contain 1 atom of substance, weighed in decigrammes per litre or in grains per 1000 dm.

A Titrated Solution (from the French word *titre*, title or power) denotes a solution whose strength or chemical power has been accurately found by experiment.

When a chemical substance or solution is directed to be *titrated*, the meaning is that it is to be quantitatively tested for the amount of pure substance it contains by the help of standard or titrated solutions. The term is used in preference to *tested* or *analyzed*, because these expressions may relate equally to qualitative and quantitative examinations, whereas titration can only apply to quantitative examination.

# ERRATA.

Page 25, 7 lines from top, for 60° read 62° Fahr.

„ 45, 6 „ „ bottom, for *a* read *b*.

„ 45, 2 „ „ „ for ammonium read caustic ammonia.

# HANDBOOK OF VOLUMETRIC ANALYSIS.

---

## PART I.

### INTRODUCTION.

§ 1. VOLUMETRIC analysis, or quantitative chemical analysis by measure, depends upon the following conditions for its successful practice :—

1. A solution of the re-agent or test, the chemical power of which is accurately known.

2° A graduated vessel from which portions of it may be accurately delivered.

3° The decomposition which the test solution produces with any given substance must be of such a character that its termination is unmistakable to the eye, and thereby the quantity of the substance with which it has combined accurately determined.

Suppose for instance that it is desirable to know the quantity of pure silver contained in a shilling. The coin is first dissolved in nitric acid, by which means a bluish solution, containing silver, copper, and probably other metals, is obtained. It is a known fact that chlorine combines with silver in the presence of other metals to form chloride of silver, which is insoluble in nitric acid. The proportions in which the combination takes

place are 35.46 of chlorine to every 108 of silver; consequently if a standard solution of pure chloride of sodium is prepared by dissolving 58.46 grains of the salt (i.e., 1 eq. sodium = 23, 1 eq. chlorine = 35.46 = 1 eq. chloride of sodium, 58.46) in so much distilled water as will make up exactly 1000 grains by measure; every single grain of this solution will combine with 0.108 grains of pure silver to form chloride of silver, which precipitates to the bottom of the vessel in which the mixture is made. In the process of adding the salt solution to the silver, drop by drop, a point is at last reached when the precipitate ceases to form. Here the process must stop. On looking carefully at the graduated vessel from which the standard solution has been used, the operator sees at once the number of grains which have been necessary to produce the complete decomposition. For example, suppose the quantity used was 520 grains; all that is necessary to be done is to multiply 0.108 grains by 520, which shews the amount of pure silver present to be 56.16 grains.

This method of determining the quantity of silver in any given solution occupies scarcely a quarter of an hour, whereas the estimation by weighing could not be done in half a day, and even then not so accurately as by the volumetric method. It must be understood that there are certain necessary precautions in conducting the above process which I have not described, those will be found in their proper place, but from this example it will at once be seen that the saving of time and trouble, as compared with the older methods of analysis, is immense; beside which, in the majority of instances in which it can be applied, it is equally accurate, in many cases much more so. For technical purposes, such as the examination of substances used in arts and manufactures, the system has been a great boon, and every day is bringing fresh applications of it both to pure and applied chemical science.

The only condition on which the volumetric system of analysis can be carried on successfully is that the greatest care

is exercised with respect to the graduation of the measuring instruments, and the strength and purity of the standard solutions. A very slight error in the analytical process becomes considerably magnified when calculated for pounds, hundred-weights, or tons of the substance tested.

The end of the operation in this method of analysis is in all cases made apparent to the eye. In alkalimetry it is the change of colour produced in litmus, turmeric, or other sensitive vegetable colouring matter. The formation of a permanent precipitate, as in the estimation of cyanogen. A precipitate ceasing to form, as in chlorine and silver determinations. The appearance of a distinct colour, as in iron analysis by permanganate solution, and so on.

I have adopted the classification of methods used by Mohr and others, namely :

1. Where the determination of the substance is effected by saturation with another substance of opposite properties,—generally understood to include acids and alkalies.

2. Where the determination of a substance is effected by a reducing or oxidising agent of known power, including most metals, with their oxides and salts; the principal oxidising agents being permanganate of potash, bichromate of potash, and iodine; and the corresponding reducing agents protoxide of iron and hyposulphite of soda.

3. Where the determination of a substance is effected by precipitating it in some insoluble and definite combination; an example of which occurs in the estimation of silver described at the commencement of this treatise.

This classification does not rigidly include all the volumetric processes that may be used, but it divides them into convenient sections for describing the peculiarity of the re-agents used, and their preparation. If strictly followed out, it would in some cases necessitate the registration of the body to be analysed under two or three heads; copper, for instance, can be determined residually by permanganate of potash; it can also be

determined by precipitation with sulphide of sodium. The estimation of the same metal by cyanide of potassium, on the other hand, would not come under any of the heads.

It will be found, therefore, that I have taken liberties with the arrangement, and for convenient reference have included all analytical processes applicable to a given body under its name.

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## THE INSTRUMENTS AND APPARATUS.

### THE BURETTE.

§ 2. OR graduated tube for delivering the standard solution, may be obtained in a great many forms, under the names of their respective inventors, such as Mohr, Gay Lussac, Binks, &c., but as some of these possess a decided superiority over others, it is not quite a matter of indifference which is used, and therefore a slight description of them may not be out of place here. The burette, with india-rubber tube and clip, contrived by Dr. Frederic Mohr of Coblenz, shewn in Figs. 1 and 2, has the preference above all others for general purposes.

The advantages possessed by this instrument are, that its constant upright position enables the operator at once to read off the number of degrees of test solution used for any analysis. The quantity of fluid to be delivered can be regulated to the greatest nicety by the pressure of the thumb and finger on the spring clip, and the instrument not being held in the hand, there is no chance of increasing the bulk of the fluid by the heat of the body, and thus leading to incorrect measurement, as is the case with Binks' or Gay Lussac's form of instrument. The principal disadvantage, however, of these two latter forms of burette is, that a correct reading can only be obtained by placing



Fig. 1.



Fig. 2.

them in an upright position, and allowing the fluid to find its perfect level. The preference should therefore, unhesitatingly, be given to Dr. Mohr's burette, wherever it can be used; the greatest drawback to it is, that it cannot be used for permanganate of potash in consequence of its india-rubber tube, which decomposes the solution.



We are again indebted, I believe, to Dr. Mohr for another form of instrument to overcome this difficulty, viz., the foot burette, with india-rubber ball, shewn in Fig. 3.

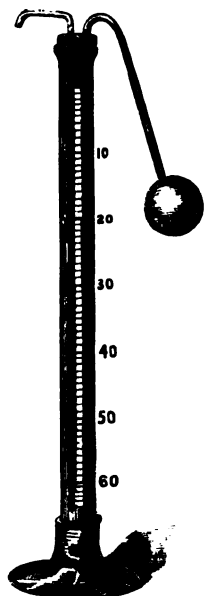


Fig. 3.



Fig. 4.

The flow of liquid from the exit tube can be regulated to a great nicety by pressure upon the elastic ball, which is of the ordinary kind sold for children, and has two openings, one cemented to the tube with shellac, and the other at the side, over which the thumb is placed when pressed, and on the removal of which it refills itself with air.

Gay Lussac's burette, supported in a wooden foot, may be used instead of the above form, by inserting a good fitting cork into the open end, through which a small tube bent at right angles

is passed. If the burette is held in the right hand, slightly inclined towards the beaker or flask into which the fluid is to be measured, and the mouth applied to the tube, any portion of the solution may be emptied out by the pressure of the breath, and the disadvantage of holding the instrument in an horizontal position, to the great danger of spilling the contents, is avoided; at the same time the beaker or flask can be held in the left hand and shaken so as to mix the fluids, and by this means the end of the operation more accurately determined.

Fig. 4 will shew the arrangement here described.

There is an arrangement of Mohr's burette which is extremely serviceable, when a constant series of analyses of the same character have to be made, such as in alkali works, assay offices, &c. It consists in having a T piece of glass tube inserted between the

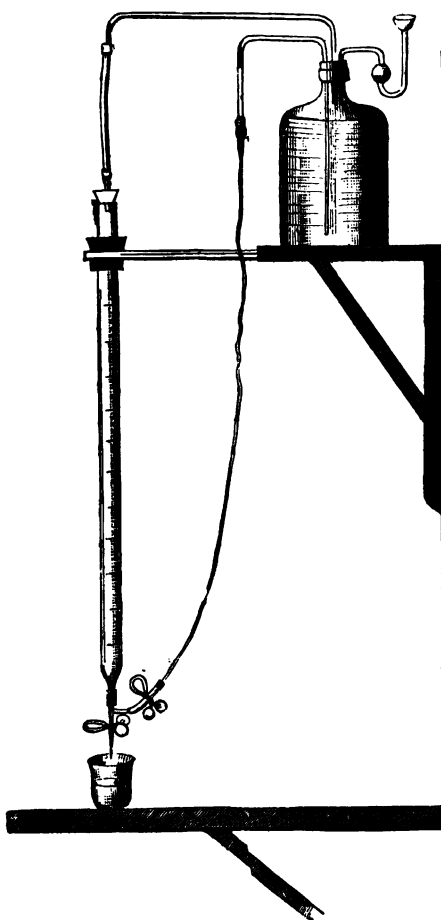


Fig. 5.

lower end of the burette and the spring clip, which communicates with a reservoir of the standard solution, placed above, so that the burette may be filled as often as emptied, by a syphon, and in so gradual a manner that no air bubbles occur, as in the case of filling it with a funnel, or pouring in liquid from a bottle; beside which, this plan prevents evaporation or dust in the standard solution either in the burette or reservoir; it is especially applicable to burettes containing caustic alkalies.

Fig. 5 shows the arrangement in detail.

Gay Lussac's burette, shewn in Fig. 6, should have a wooden support or foot into which it may be inserted, so as to be read correctly. By using it in the following manner, its natural disadvantages may be overcome to a great extent. Having fixed the burette into the foot securely, and filled it, take it up by the foot with the left hand, and resting the upper end upon the edge of the beaker into which the solution to be tested is placed, drop the test fluid from the burette, meanwhile stirring the contents of the beaker with a glass rod held in the right hand; by a slight elevation or depression of the left hand, the flow of test liquid is regulated until the end of the operation is secured, thus avoiding the annoyances which arise from alternately placing the instrument in an upright and horizontal position.



Fig. 6.

Geissler's burette differs from Gay Lussac's in having the fine tube enclosed within the large one, but as it is a difficult instrument to make, it has not found much favour.

Binks', or as it is sometimes called, the English burette, is well known, and need not be described; it is the least recommendable of all forms, in my opinion.

It is most convenient to have burettes graduated to 25 or 30 CC in  $\frac{1}{10}$ , 55 or 60 CC in  $\frac{1}{2}$  and 110 CC in  $\frac{1}{4}$ .

#### THE PIPETTE.

§ 3. THE pipettes used in volumetric analysis are of two kinds, viz., those which deliver one certain quantity only, and those which are graduated so as to deliver various quantities at the discretion of the analyst. In the former kind, or whole

pipette, the graduation may be of three kinds, namely, 1st, in which the fluid is suffered to run out by its own momentum only.

2nd, in which it is blown out by the breath. 3rd, in which it is allowed to run out to a definite mark. Of these methods the last is preferable in point of accuracy, and should therefore be adopted if possible. The next best form is that in which the liquid flows out by its own momentum, but in this case the last few drops empty themselves very slowly, but if the lower end of the pipette be touched against the beaker or other vessel into which the fluid is poured, the flow is hastened considerably, and in graduating the pipette, it is preferable to do it on this plan.

In both the whole and graduated pipettes, the upper end is narrowed to about  $\frac{1}{8}$  inch, so that the pressure of the moistened finger is sufficient to arrest the flow at any point.

Fig. 7 shews two whole pipettes, one of small and the other of large capacity, and also a graduated pipette of medium size.

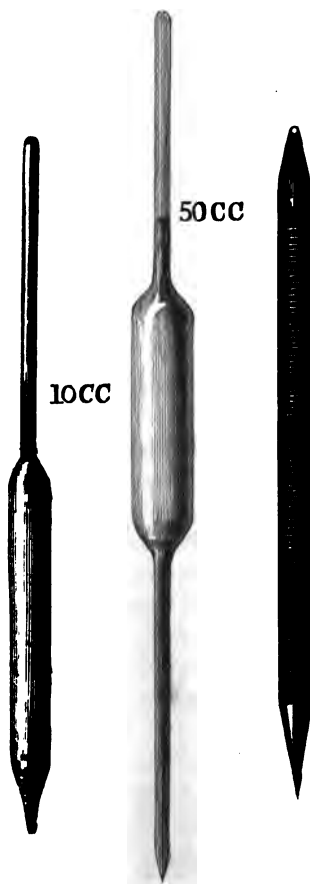


Fig. 7.

### THE MEASURING FLASKS

§ 4. THESE indispensable instruments are made of various capacities; they serve to mix up standard solutions to a given volume, and also for the subdivision of the substance to be tested by means of the pipettes, and are in many ways most convenient. They should be tolerably wide at the mouth, and have a well-ground glass stopper, and the graduation line should fall just below the middle of the neck, so as to allow room for shaking up the fluid.

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### ON THE CORRECT READING OF GRADUATED INSTRUMENTS.

§ 5. THE surface of liquids contained in narrow tubes is always curved, in consequence of the capillary attraction exerted by the sides of the tube, and consequently there is a difficulty in obtaining a distinct level in the fluid to be measured. If, however, the lowest point of the curve is made to coincide with the graduation mark, a correct proportional reading is always obtained, hence this method of reading is the most satisfactory.



Fig. 8.

Professor Erdmann has contrived a useful little instrument to accompany Dr. Mohr's burette, which gives the most accurate reading that can be obtained; its form is shewn in Fig. 8, and is known by the name of Erdmann's float. It consists of an elongated glass bulb, rather smaller in diameter than the burette itself, and is weighted at the lower end with a globule of mercury, like an hydrometer; it is drawn to a point at the upper end, and the point is bent round

so as to form a small hook, by means of which it can be lifted in and out of the burette with a bent wire ; a line is made with a diamond round its middle by means of a lathe, and the coincidence of this line with the graduation mark of the burette is accepted as the true reading. The actual height of the liquid in the burette is not regarded, because if the operator be-

gins with the line on the float, opposite the 0 graduation mark on the burette, the same proportional division is always maintained.

To prevent evaporation and the entrance of dust in Mohr's burette, the inventor recommends a round and well polished marble, such as boys play with, to be laid on the open end ; and I have myself found it more satisfactory than anything else. In burettes containing caustic alkaline solutions, a cork with carbonic acid tube should be used.

Beside the measuring flasks, it is necessary to have graduated vessels of cylindrical form, for the purpose of preparing standard solutions, &c.

Fig. 9 shews a stoppered cylinder for this purpose, generally called a test mixer.

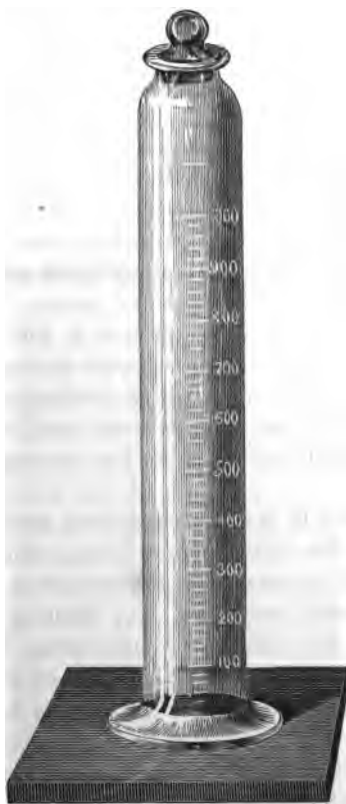


Fig. 9.

ON THE SYSTEM OF WEIGHTS AND MEASURES TO BE ADOPTED  
IN VOLUMETRIC ANALYSIS.

§ 6. It is much to be regretted that the decimal system of weights and measures used on the continent is not universally adopted, for scientific and medicinal purposes, in England. I am glad to find that among many of our leading professional chemists it is now used, and growing daily more and more into favour. In scientific investigations, the importance of a cosmopolitan system of weights and measures cannot be overrated, and the anomalies produced by our arbitrary sets of pounds, ounces, and drachms, would be ludicrous, were it not for the great confusion which they engender. These annoyances are increased by the fact, that the valuable chemical researches of our neighbours the French, Germans, Dutch, and Belgians, are conducted on a different system to our own; and although we remove the difficulty, to a certain extent, by using the grain as a unit of weight and measure, its small capacity renders its use awkward when large quantities are concerned, because it necessitates six or eight figures in the place of two or three, or even less; and not only more trouble to record and calculate, but far more difficult to remember.

The great advantage possessed by the French decimal system is its uniformity throughout. The unit of weight is the gramme, ( $= 15.43235$  grains troy,) and a gramme of distilled water at  $39^{\circ}$  Fahr. measures exactly a cubic centimètre. The kilogramme contains 1000 grammes. The litre 1000 cubic centimètres.

There is no effort of memory needed in the use of this system, as when once understood it is so simple that none but the veriest dolts could mystify it.

I therefore should unhesitatingly advise all chemical students to commence with the use of it, or at least to make themselves fully acquainted with its principles, so as to be able to calculate the one system into the other, if necessary.

It may not be out of place here to give a short description of the origin of the French decimal system, now used exclusively for scientific purposes in that country, and also in Prussia, Austria, Holland, Sweden, Denmark, Belgium, and Spain. If it should assist in bringing it more extensively into use in our own country, I shall rejoice.

The commission appointed after the revolution in France for the purpose of instituting a decimal system of weights and measures, founded their standard on the length of the meridian arc between the pole and equator, the ten millionth part of which was called the *mètre*, ( $=39\cdot3710$  English inches,) although the accuracy of this measurement has since been disputed. It would have been preferable, as since proposed, that the length of a pendulum vibrating exactly 86,400 times in twenty-four hours, or one second for each vibration, equivalent to  $39\cdot1372$  English inches, should have been taken as the standard *mètre*, in which case it would have been much easier to verify the standard in case it should be damaged or destroyed. However, the actual *mètre* in use is equal to  $39\cdot371$  inches, and from this standard its multiples and subdivisions all proceed decimally, its one tenth part being the *decimètre*, one hundredth the *centimètre*, and one thousandth the *millimètre*.

In like manner a cube of distilled water at its greatest density, viz.,  $39^{\circ}$  Fahr., or  $4^{\circ}$  Centigrade, whose side measures one *decimètre*, weighs one *kilogramme*, or 1000 grammes, and occupies the volume of 1 litre, or 1000 cubic centimètres.

This simple relationship between liquids and solids is of great value in a system of volumetric analysis, and even for ordinary analysis by weight; for technical purposes it is equally as applicable as the grain system, the results being invariably tabulated in percentages. Complete tables of these weights and measures will be found at the end of the book.

With these brief explanations, therefore, I have only to state that the French decimal system will be mainly used throughout this treatise, but at the same time those who may desire to



adhere to the ordinary grain weights, can do so without interfering with the accuracy of the processes described.

As has been before stated, the true cubic centimeter contains one gramme of distilled water at its greatest density, viz., 4° Centigrade, or 39° Fahr., but as this is a degree of temperature which it is impossible to work at for more than a month or two in the year, and even then not comfortably, it is better to take the temperature of 62° Fahr., or about 16.5 Cent. as the standard, because in winter most laboratories or rooms have furnaces or other means of warmth, and in summer the same localities would not, under ordinary circumstances, have a much higher degree of heat than 62°. In order, therefore, that the graduation of instruments on the metrical system may be uniform with our own fluid measures, the cubic centimeter must contain one gramme of distilled water at 62°. The true CC, (i.e., = 1 Gm. at 39° Fahr.,) contains only 0.999 Gm. at that temperature; but for convenience of working, and for uniformity with our own standards of volume, it is better to make the CC contain one gramme at 62° Fahr. The real difference is one thousandth part. The operator, therefore, supposing he desires to graduate his own measuring flasks, must weigh into them 250, 500, or 1000 grammes of distilled water at 62° Fahr. Of course it must be understood that these vessels are to *contain* their respective volumes only, and not to *deliver* them if poured out, consequently they must be carefully dried before weighing the water into them.

The accurate graduation of burettes and pipettes can only be done by carefully constructed machines, and is, therefore, generally speaking, beyond the compass of the analyst himself; nevertheless, they should be carefully tested by him before being used, as, unfortunately, they do not always possess the accurate measurement to which they pretend. In the verification of both burettes and pipettes, it is only necessary to allow ten cubic centimeters of distilled water to flow into a dry and accurately tared flask or beaker. If the weight at 62° is

ten grammes, it is sufficient; the next ten grammes may be tried in like manner, and so on until the entire capacity is proved.

Beside the litre flask, it is advisable to have flasks graduated for 100, 200, 250, 300, and 500 CC, as they are extremely serviceable in dividing small quantities of substance into still smaller proportional parts. Suppose, for instance, it is desired to take the tenth part of a solution for the purpose of separating any single constituent, let it be put into a 200 CC flask, and filled to the mark with water, and well shaken; 20 CC taken out with a pipette will at once give the quantity required.

Burettes, pipettes, and flasks may also be graduated in grains, in which case it is best to take 10,000 grains as the standard of measurement. In order to lessen the number of figures used in the grain system, so far as liquid measures are concerned, I propose that 10 fluid grains be called a decem, or for shortness dm.; this term corresponds to the cubic centimeter, bearing the same proportion to the 10,000 grain measure as the cubic centimeter does to the litre, namely, the one thousandth part. The use of a term like this will serve to prevent the number of figures, which are unavoidably introduced, by a small unit like the grain.

I am aware that the term decem has been used by Mr. Acland to represent the tenth part of a gallon; but I apprehend there is no fear of confounding the two from the vast difference in their capacity. It is quite an arbitrary term, and does not carry its value in its name like the cubic centimeter, but I can think of no simpler or better method of bringing the grain system to the same kind of arrangement as that of the gramme.

The utility of it is principally apparent in the analysis for percentages, particulars of which will be found hereafter.

The 1000 grain burette or pipette will, therefore, contain 100 decems, the 10,000 grain measure, 1000 dm., and so on.

The capacities of the various instruments graduated on the grain system may be as follows:—

Flasks 10,000, 5,000, 2,500, and 1000 grs., = 1000, 500, 250, and 100 dm. Burettes 300 grains in 1 grain divisions, for very delicate purposes = 30 dm. in  $\frac{1}{10}$ ; 600 grain in 2-grain divisions, or  $\frac{1}{2}$  dm.; 1100 grain in 5-grain divisions, or  $\frac{1}{2}$  dm.; 1100 grain in 10-grain divisions, or 1 dm. The burettes are graduated above the 500 or 1000 gr., in order to allow of analyses for percentages by the residual method. Whole pipettes to deliver 10, 20, 50, 100, 200, 500, and 1000 grains; graduated ditto, 100 gr. in  $\frac{1}{10}$  dm.; 500 grs. in  $\frac{1}{2}$  dm.; 1000 grs. in 1 dm.

Of course it will be readily seen that this method of division is not absolutely necessary; it is only given here as being, in my opinion, the most convenient for general purposes.

Those who may desire to use the decimal systems constructed on the gallon measure = 70,000 grains, will bear in mind that the "septem" of Mr. Griffin, or the "decimillem" of Mr. Acland, are each equal to 7 grains, and therefore bear the same relation to the pound = 7,000 grs., as the cubic centimeter does to the litre, or the decem to the 10,000 grs. An entirely different set of tables for calculations, etc., is required for these systems, but the analyst may readily construct them when once the principles contained in this treatise are understood.

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#### VOLUMETRIC ANALYSIS ON THE ATOMIC SYSTEM AND THE PREPARATION OF NORMAL TITRATED SOLUTIONS.

§ 7. WHEN analysis by measure first came into use, the test solutions were generally prepared so that each substance to be tested had its own special re-agent; and the strength of the standard solution was so calculated as to give the result in percentages. Consequently, in alkalimetry a distinct standard acid

was used for soda, another for potash, a third for ammonia, and so on, necessitating a great variety of standard solutions.

John Joseph Griffin, the well-known and talented maker of chemical apparatus, and Dr. Andrew Ure, appear to have been the first to suggest the use of standard test solutions based on the atomic system, and following in their steps Mohr has worked out a most elaborate and extensive system of analysis, which must be an inestimable boon to all who concern themselves with scientific and especially technical chemistry. Not only has Mohr done this, but in addition to it, has enriched his processes with so many original investigations and improved the necessary apparatus to such an extent, that he may with justice be called the father of the volumetric system.

His "*Lehrbuch der Chemisch Analytischen Titrimethode*," is the most complete treatise on the subject, and well-deserving the thanks of all students of the science.

But to return to the explanation of the system, the standard (or titrated, from the French word *titre*, strength) solutions are so prepared as to contain an atom of the required test, weighed in thousandths of the entire solution. For instance, suppose it is desired to prepare a normal alkaline solution for acidimetry, the atomic weight of carbonate of soda is 53, therefore 53 Gm. of pure and dry carbonate of soda are weighed, introduced into a litre flask and dissolved, so as to make exactly the measure of 1 litre. It is manifest that every 100 CC of this solution will contain 5.3 Gm. of carbonate of soda, and every 10 CC, 0.53 Gm. Therefore 100 CC will exactly neutralize 4.0 Gm. of anhydrous sulphuric acid, or 10 CC 0.4 Gm., and so on.

In like manner, if 1000 grains are used as the standard measure in place of the litre, 53 grains of carbonate of soda would be used; or as 1000 grains is too small a quantity to make, it is better to weigh 530 grains to 10,000. The solution would then have exactly the same strength as if prepared on the litre system, as it is proportionally the same in chemical power; and

either solutions may be used indiscriminately for instruments graduated on both scales, bearing in mind that the substance to be tested with a CC burette, must be weighed on the Gramme system, and *vice versa*, unless it be desired to calculate one system of weights into the other.

Of the standard solution so prepared, 1 litre should, of course, exactly saturate the atomic weight in grammes of any acid capable of decomposing the carbonate of soda, namely,—40 Gm. of anhydrous, or 49 Gm. of monohydrated sulphuric acid, 54 Gm. of anhydrous nitric, or 36.46 Gm. of anhydrous hydrochloric acid, etc. In like manner, a standard solution of oxalic acid, containing 63 grains of the crystallized acid, in 1000 grains of solution, will saturate exactly 31 grains of pure caustic soda, 47.11 grs. of potash, 28 grs. of lime, or 17 grains of ammonia, etc., consequently it will be seen at once that one standard acid will serve for the estimation of a variety of alkalies, and one standard alkali for a like variety of acids; supposing, therefore, it is desired to ascertain the percentage of real carbonate of soda in a given sample of commercial alkali, all that is necessary is to weigh 5.3 Grammes, or  $\frac{1}{10}$  atom of it, dissolve it in water, add a few drops of tincture of litmus, and from a 100 CC burette allow the standard acid to flow until the point of saturation is reached. If 90 CC are required to produce this re-action, the sample contains 90 per cent. of real carbonate of soda.

In the same way, 53 grains of the alkali would require 90 decems or 900 grains of acid, which would likewise be 90 per cent.

Or suppose the analyst desires to know the percentage of real caustic soda, free and combined, contained in the sample of alkali, without calculating it from the carbonate found as above, 3.1 Gm., or  $\frac{1}{10}$  atom is treated as before, and the number of CC required is the percentage of real alkali. In the same sample 52.6 CC would be required = 52.6 per cent. of real alkali, or 90 per cent. of carbonate. Beside the test solutions containing

an atom in Grammes per litre, or in grains per 100 decems, it is advisable to have others  $\frac{1}{10}$  that strength, so that greater delicacy may be obtained in certain cases. Standard solutions of the former kind are called normal, and of the latter decinormal, or, for shortness, N and  $\frac{N}{10}$  respectively. The decinormal solutions may be made either by weighing  $\frac{1}{10}$  atom of the test direct and diluting to 1000, or by diluting 100 parts of the normal solution to 1000.

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**RULES FOR OBTAINING THE PERCENTAGE OF A SUBSTANCE  
WITHOUT CALCULATION.**

§ 8. 1. *With normal solutions  $\frac{1}{10}$  atom in grammes, or 1 atom in grains, of the substance tested is to be weighed, and the number of cubic centimeters or decems required is the percentage of the substance whose atomic weight has been used.*

2. *With decinormal solutions  $\frac{1}{100}$  atom in grammes, or  $\frac{1}{10}$  atom in grains, of the substance tested is to be weighed, and the number of cubic centimeters or decems required is the percentage of the substance whose atomic weight has been used.*

It now only remains to say, with respect to the system of weights and measures to be used, that the analyst is at liberty to choose his own plan. Both systems are susceptible of equal accuracy, and he must study his own convenience as to which he will adopt.

The normal solutions prepared on the gramme system are equally applicable for that of the grain, and *vice versâ*, so that there is no necessity for having distinct solutions for each system. It frequently occurs that, from the nature of the substance, or from its being in solution, this percentage method cannot be conveniently followed. For instance, suppose the operator has a solution containing an unknown quantity of caustic potash, the strength of which he desires to know; a weighed or measured quantity of it is brought under

the acid burette and saturated exactly by aid of litmus; 32 CC were required. The calculation is as follows:—  
As 100 CC are to 4.711 Gm. KO, so are 32 CC to  

$$x \frac{4.711 \times 32}{100} = 1.507 \text{ Gm. KO.}$$

The simplest way, therefore, to proceed, is to multiply the number of CC of test solution required in any analysis, by the  $\frac{1}{1000}$  of the atomic weight of the substance sought, which gives at once the figures required.

An example may be given—1 Gm. of marble or limestone is taken for the estimation of pure carbonate of lime and exactly saturated with standard nitric acid—(sulphuric or oxalic acid are of course not admissible) 17.5 CC were required, therefore,  $17.5 \times 0.050$  (the  $\frac{1}{1000}$  of the atomic weight of  $\text{CaO}, \text{CO}_2$ ) gives 0.875 Gm., and as 1 Gm. of substance only was taken = 87.5 % carbonate of lime. The multiplication may also be dispensed with if desired and addition substituted by constructing tables on the following system—1 CC of normal standard acid is equal to 0.04711 Gm. KO.

Cubic Centimeters.

	1	2	3	4	5	6	7	8	9
Pure Potash	·04711	·09422	·14133	·18844	·23555	·28266	·32977	·37688	·42399

If we used this table instead of the equation given above for the estimation of potash in solution, the result would be the same, viz.—

30 CC = 1.41330 Gm. (Column 3 the decimal point  
 2 CC = 0.09422 Gm. [one place to the left.]  
 1.50752 Gm. KO.

In some cases it is necessary to have standard solutions based on an empirical instead of an atomic system, in which case each solution only suffices for the estimation of one special substance. This is the case in the analysis of urine and a few other substances, particulars of which will be found in their proper places.

There are other test solutions which, in consequence of their proneness to decomposition, cannot be kept at any particular strength for a length of time, consequently they must be tested themselves previous to being used. Permanganate of potash and sulphurous acid are examples of such solutions. They will also be described under their respective heads.

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**ON THE DIRECT AND INDIRECT PROCESSES OF ANALYSIS  
AND THEIR TERMINATION.**

§ 9. The direct method includes all those analyses where the substance under examination is decomposed by simple contact with a known quantity or equivalent proportion of some other body capable of combining with it, and where the end of the decomposition is manifested in the solution itself.

It also properly includes those analyses in which the substance re-acts upon another body to the expulsion of a representative equivalent of the latter, which is then estimated as a substitute for the thing required.

Examples of the first kind are readily found in the process for the determination of iron by permanganate of potash, where the beautiful rose colour of the permanganate asserts itself as the end of the re-action.

The testing of acids and alkalies comes, also, under this class, the great sensitiveness of litmus allowing the most trifling excess of acid or alkali to alter its colour. The second is exemplified in the analysis of bin-oxide of manganese, and also other peroxides and oxygen acids, by boiling with hydrochloric acid. The chlorine evolved is estimated as the equivalent of the quantity of oxygen which has displaced it. We are indebted to Bunsen for a most accurate and valuable series of processes based on this principle.



The indirect or residual method is such that the substance to be analysed is not estimated itself, but the excess of some other body added for the purpose of combining with it or of decomposing it, and the quantity or strength of the body added being known, and the conditions under which it enters into combination being also known, by deducting the remainder or excess (which exists free) from the original quantity, it gives at once the proportional quantity of the substance sought.

An example will make the principle obvious :—Suppose that a sample of either native carbonate of lime, baryta, or strontian is to be tested. It is not possible to estimate them with standard nitric acid in the exact quantity they require for decomposition. There must be an excess of acid and heat applied also to get them into solution, if, therefore, a known excessive quantity of standard acid be first added, and solution obtained, and the liquid then titrated backward with litmus and standard alkali, the quantity of free acid can be exactly determined, and consequently that which is combined also.

In some analyses it is necessary to add a substance which shall be an indicator of the end of the process; such for instance is litmus in alkalimetry, chromate of potash in silver and chlorine, and starch in iodine, estimations.

There are other processes, the end of which can only be determined by an indicator separate from the solution, such is the case in the estimation of iron by bichromate of potash, where a drop of the liquid is brought into contact with another drop of solution of red prussiate of potash on a white slab or plate, when a blue colour ceases to form, by contact of the two liquids the end of the process is reached.

The latter is somewhat less reliable, in point of delicacy, than the others, but nevertheless, with care and practice, is susceptible in most cases of very tolerable accuracy.

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## PART II.

## ANALYSIS BY SATURATION.

## ALKALIMETRY.

§ 10. GAY LUSSAC based his system of alkalimetry upon a titrated solution of carbonate of soda, with a corresponding solution of sulphuric acid, and as this was devised mainly for the use of soda manufacturers it was doubtless the best system for that purpose. It possesses the recommendation that a pure standard solution of carbonate of soda can be more readily obtained than any other form of alkali. Dr. Mohr has introduced the use of caustic alkali instead of a carbonate, the strength of which is established by a standard solution of oxalic acid, containing 63 Gm. or 1 atom to the litre. The principal advantage in the latter system is, that in testing the strength of acids with a caustic alkali, the well-known interference produced by carbonic acid is avoided. The caustic solutions of soda or potash are difficult to preserve so as to prevent their absorbing carbonic acid; another disadvantage is, that it is exceedingly difficult to procure or manufacture caustic soda or potash perfectly pure, and ammonia is volatile at ordinary temperatures, and rendered much more so by being heated. These drawbacks can however be, to a great extent, overcome by special means, and, in laboratories for general investigations, it is advisable to employ both systems.

In testing both acids and alkalies it is necessary to employ a solution of litmus as indicator, which is best prepared by powdering about half an ounce of the solid material, and digesting it with half a pint of distilled water for a few hours in a warm place, decanting the clear liquid from the sediment, adding, if necessary, a few drops of dilute nitric acid so as to produce a violet colour, and preserving it in a bottle with an open glass tube passed through the cork. If corked up closely it changes colour, and is not nearly so sensitive as when exposed to the air. When litmus is prepared and kept in this manner, the very faintest excess of acid or alkali is sufficient to produce either a distinct red or blue, in a dilute solution.

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#### PREPARATION OF THE NORMAL ACID AND ALKALINE SOLUTIONS.

##### Normal Carbonate of Soda.

§ 11. THE solution of carbonate of soda must contain 53 Gm. of the pure and freshly-ignited salt in the litre, or 530 grains in the 10,000 grain measure, according to the system used. If this salt is not ready at hand it is best to prepare it as follows :

A convenient quantity of the purest commercial bicarbonate of soda, (the kind prepared by Messrs. Howard and Sons, of Stratford, I have found to answer best,) is to be placed in a funnel upon an ordinary paper filter, and washed with cold distilled water until all traces of chlorides and sulphates have disappeared in the filtrate, then put into a slightly warm place to dry.

About 85 Gm. of this, washed and dried bicarbonate, are to be heated to dull redness in a platinum, silver, or porcelain crucible, for about ten minutes, then placed under an

exsiccator to cool; when placed upon the balance it will be found that very little more than 53 Gm. remain. The excess is to be removed as quickly as possible, and the contents of the crucible emptied into a beaker, then wash out the crucible into the beaker, and as soon as the salt is dissolved, decant the solution into a litre flask and make up the litre exactly with distilled water, at 60 Fahr.

#### Normal Sulphuric Acid.

About 30 CC of pure sulphuric acid of s. g. 1.840, or thereabouts, are mixed with three or four times the volume of distilled water and allowed to cool, then put into the graduated cylinder and diluted up to the litre. It must now be tested by the normal alkali, which is best done by putting 10 CC of the latter into a small beaker or flask with litmus, and from a 10 or 12 CC pipette, divided in  $\frac{1}{10}$  CC, allowing the acid to flow until the point of neutrality is reached. If more than 10 CC are required the acid is too weak, if less, too strong. If the acid from which the solution was made was of the spec. grav. mentioned, it will generally be too strong, which is preferable. Suppose, therefore, it required 8.9 CC to saturate the 10 CC of alkali, 890 CC will be required to make one litre of standard acid; remove, therefore, the excess from the cylinder and dilute to exactly one litre. Now test again with the pipette, if the previous examination was correct, 10 CC of each solution should exactly neutralize each other.

The acid may also be tested by precipitation with chloride of barium, in which case 10 CC should produce as much sulphate of baryta as is equal to .40 Gm. of anhydrous sulphuric acid, or 40 Gm. per litre.

#### Normal Oxalic Acid.

This solution possesses the great advantage that it may be established direct, by weighing 63 Gm. or 1 atom of the purest acid in a litre of water, or 630 grains to 1000 decems.

The acid must have been recrystallized several times and not in the slightest effloresced. The solution keeps well and will bear heating without volatilizing the acid.

#### Normal Caustic Alkali

May consist of either soda, potash, or (less recommendably) ammonia. The two first are best prepared from the pure carbonate by the aid of fresh-burnt lime.

Potash is preferred to soda by Mohr, as it has less effect upon the glass burettes and pipettes in which it is used. One part of pure carbonate of potash, prepared from good cream of tartar or the same of carbonate of soda, is to be dissolved in 10 parts of distilled water and boiled in a clean iron pot, during the boiling strong and fresh milk of lime is to be added and boiled until all the carbonic acid is removed. Half the weight of the potash or soda in lime is sufficient; cover the vessel closely and set aside to cool and settle; when cold, the clear supernatant liquid is to be tested by normal oxalic or sulphuric acid, and made of the proper strength as directed for sulphuric acid.

The best method of preserving the solution is shewn in Fig. 10, first suggested, I believe, by Professor Graham. The



Fig. 10.

tube inserted through the cork contains a mixture of equal parts of Glauber's salt and quicklime, previously dried and ignited gently together.

Burettes may also be fitted with this carbonic acid tube, by which means the alkaline solutions may be kept in them a long time without deteriorating. By the help of this normal alkali, or the normal carbonate of soda, it is easy to prepare normal nitric and hydrochloric acids. Normal nitric acid is especially serviceable for the analysis of the alkaline earths, such as limestones, marls, chalks, and the native carbonates of baryta, strontia, etc.

Mohr suggests that both acid and alkaline test solutions should have litmus added to them when prepared, so as to avoid any mistake in using them, as in that case all alkaline solutions would be blue, and acid, red. The suggestion is a good one, but care, of course, must be taken that the volume of litmus solution is included in the litre, and not subsequently added so as to weaken the strength of the solutions.

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#### METHOD OF PROCEDURE IN TESTING ALKALIES.

§ 12. THE necessary quantity of substance being weighed, it is dissolved in distilled water, and if any sediment remains the solution is filtered, and the filter thoroughly washed, the washings being received into the vessel containing the filtrate; add a sufficient quantity of litmus to produce a distinct blue colour, and allow the normal acid to flow from the burette until a claret tinge begins to appear. In the case of carbonates this takes place some time before the complete quantity of acid is added, owing to the liberation of carbonic acid. In order to

dissipate the carbonic acid, the liquid must be heated to boiling, when the blue colour will again appear. Continue to add the acid a few drops at a time, and repeat the heating until all the carbonic acid is expelled and a distinct red colour is produced in the liquid by the final drop of acid. It is always advisable to make a second and conclusive test of the alkali, and, therefore, the first supplies a guide to the quantity of acid required, and allows a more exact method of procedure towards the end of the process.

In the examination of samples of ordinary soda or pearlash, I have always found it advisable to proceed as follows:—

Powder and mix the sample thoroughly, and put into a stoppered bottle, weigh 10 Gm. in a platinum or porcelain crucible, and ignite gently over a spirit or gas lamp, and allow the crucible to cool under the exsiccator. Weigh again, the loss of weight gives the moisture, wash the contents of the crucible into a beaker, dissolve and filter if necessary, and dilute to the exact measure of 500 CC with distilled water in a  $\frac{1}{2}$  litre flask, after mixing it thoroughly take out 50 CC = 1 Gm. of alkali with a pipette, and empty it into a small flask, bring the flask under a burette containing normal acid and graduated to  $\frac{1}{10}$  CC, allow the acid to flow cautiously as before directed, until the neutral point is reached, the process may then be repeated, several times if necessary, in order to be certain of the correctness of the analysis.

As the presence of carbonic acid always tends to confuse the exact end of the process, the difficulty may be overcome by allowing more acid than is needed to flow into the alkali, boiling to expel the carbonic acid, and then cautiously adding normal caustic alkali, drop by drop, until the liquid suddenly changes to violet blue; by deducting the quantity of caustic alkali from the quantity of acid originally used, the exact volume of test acid necessary to saturate the 1 Gm. of alkali is ascertained.

This residual or backward method of testing gives a very sharp and sure result, as there is no carbonic acid present to interfere with the colour of the liquid. An example will make the plan clear:—

50 CC of the solution of alkali prepared as directed, and which is equal to 1 Gm. of the original sample, is put into a flask and exactly 20 CC of normal acid allowed to flow into it, it is then boiled and shaken till all carbonic acid is expelled, and normal caustic alkali added backward till the neutral point occurs; the quantity required was 3·4 CC, which deducted from 20 CC of acid, leaves 16·6 CC. The following calculation therefore gives the percentage of real alkali supposing it to be soda—31 is the equivalent of soda, and 1 CC of the acid is equal to ·031 Gm. of real alkali, (NaO) therefore, 16·6 CC is multiplied by ·031, which gives ·5146, and as 1 Gm. was taken the decimal point is moved two places to the right, which gives 51·46 per cent. of real alkali; if calculated as carbonate the 16·6 would be multiplied by ·053, (53 being the equivalent of  $\text{NaO CO}_2$ ) which gives ·8798 grm. = 87·98 per cent.

In the preparation of standard solutions it is exceedingly difficult to make them so exact in strength that the precise quantity, to a drop or two, shall neutralize each other, but in scientific investigations it is of the greatest importance that the utmost accuracy should be obtained; it is, therefore, advisable to ascertain the actual difference and to mark it upon the vessels in which the solutions are kept, so that a slight calculation will give the exact result.

Suppose, for instance, that a standard sulphuric acid is prepared which does not rigidly agree with the normal carbonate of soda, not at all an uncommon occurrence, as it is exceedingly difficult to hit the precise point, but in order to find out the exact difference about 3 Gm. of absolutely pure bicarbonate of soda is to be ignited in a platinum crucible until converted into mon carbonate, then placed under the exsiccator and



allowed to cool; when placed on the balance, suppose the weight found to be 1.9 Gm., it is then dissolved and titrated with the standard acid, of which 36.1 CC were required to reach the exact neutral point.

If the acid were rigidly exact it should require 35.85 CC; in order, therefore, to find the factor necessary to bring the quantity of acid used in the analysis to the normal strength, the number of CC used must be divided by the number which should have been used had the acid been strictly normal, consequently—

$$\frac{35.85}{36.1} = .993$$

.993 is therefore the factor by which it is necessary to multiply the number of CC of that particular acid used in any analysis in order to reduce it to normal strength, and should be marked upon the bottle in which it is kept.

On the other hand, suppose that the acid is too strong, and that 35.2 CC were required instead of 35.85.

$$\frac{35.85}{35.2} = 1.0184$$

1.0184 is therefore the factor by which it is necessary to multiply the number of CC of that particular acid in order to bring it to the normal strength.

It is, of course, taken for granted that the original normal solution, from which the others are graduated, shall be rigidly exact, otherwise considerable errors will inevitably occur at every step.

The following table is given as an example of the two systems of measurement which may be adopted in volumetric analysis—

Table for Alkalies.

Substance.	Formula.	Atomic Weight	Quantity to be weighed so that 1 CC or 1 dm. of normal acid = 1 per cent. of substance.	Normal Factor.*
<b>Sodium Na=23.</b>				
Caustic Soda (anhydrous)	NaO	31	3.1 Gm., or 31. grn.	0.031, or 0.31
Carb. of Soda (ditto) ...	NaO CO <sub>2</sub>	53	5.3 Gm., or 53. grn.	0.053, or 0.53
Cryst. Carb. of Soda ...	NaO CO <sub>2</sub> +10aq	143	14.3 Gm., or 143. grn.	0.143, or 1.43
Bicarbonate of Soda ...	NaO 2 CO <sub>2</sub> +HO	84	8.4 Gm., or 84. grn.	0.084, or 0.84
<b>Potassium K=39.11.</b>				
Caustic Potash .....	KO	47.11	4.711 Gm., or 47.11 grn.	0.04711, or 0.4711
Carbonate of ditto .....	KO, CO <sub>2</sub>	69.11	6.911 Gm., or 69.11 grn.	0.06911, or 0.6911
Bicarbonate of ditto ...	KO, 2CO <sub>2</sub>	100.11	10.11 Gm., or 101.1 grn.	0.1011, or 1.011
<b>Ammonium.</b>				
Ammonia .....	NH <sub>3</sub>	17	1.7 Gm., or 17.0 grn.	0.017, or 0.170
Chloride of Ammonium	NH <sub>3</sub> Cl H	53.46	5.346 Gm., or 53.46 grn.	0.05346, or 0.5346

\* This is the coefficient by which the number of CC of normal solution used is to be multiplied, in order to obtain the corresponding amount of substance examined.

## SODA.

## Examples of Analysis.

§ 13. 1. 8.4 Gm. of Howard's pure bicarbonate of soda was carefully weighed, brought into solution, and a few drops of litmus added; 105 CC of normal sulphuric acid was allowed to flow into the solution from the burette, and heated till all carbonic acid was expelled, it was then titrated backward with normal caustic alkali, of which 5.5 CC were required to reach

the neutral point, the real quantity of acid, therefore, was 99.5 CC, or  $99\frac{1}{2}$  per cent. of pure bicarbonate.

2. In like manner 53 grains of exsiccated commercial carbonate of soda was taken for examination, and 105 decems (= 1050 grains) of normal acid added, then titrated backward with 6.4 decems (= 64 grains) of normal alkali; the quantity of acid was, therefore, 98.6 decems, or 98.6 per cent. of real carbonate.

3. Ten Gm. of the same carbonate as No. 2, was dissolved in distilled water, and the solution made up to 500 CC =  $\frac{1}{2}$  litre. From this solution 50 CC = 1 Gm. of the carbonate was removed with the pipette, put into a small flask, and 24 CC of normal acid added, then titrated backward with 5.4 CC of normal alkali, the quantity of acid was, therefore, 18.6 CC, and this multiplied by .053, (1 CC of acid being equal to .053 Gm., NaO CO<sub>2</sub>) gave 98.58 per cent. of carbonate.

To those who are expert in analysis it is not necessary to take any even or exact quantity of substance for examination, as a slight calculation will give the same results as in the foregoing examples. For instance, in testing deliquescent substances, such as hydrates or monocarbonates of potash or soda, it is not advisable to protract the weighing, as the absorption of moisture vitiates the results, therefore, if a portion is placed at once into a tared watch glass or crucible, the exact weight can be more quickly ascertained than by making up or reducing the substance to any particular quantity.

4. Suppose, therefore, that a small lump of commercial hydrate of soda is placed upon the balance and found to weigh 2.657 Gm., it is transferred to a beaker and dissolved, then titrated with normal acid to the point of saturation—64 CC were required, therefore, as 1 CC is equal to .04 Gm. of pure NaO + HO · 64 CC = 2.46 Gm., which was the quantity of pure hydrate contained in the sample; the percentage is therefore arrived at by the following equation—

$$2.657 : 100 :: 2.46 : x = 92.58 \%$$

In technical examinations the operator may desire to dispense with the alkaline solution for residual titration, in which case he must proceed cautiously with the addition of normal acid towards the end of the process, (taking care to expel all the carbonic acid,) till the exact neutral point is reached.

The commercial carbonate of soda, generally called alkali, and consisting of a mixture of carbonate and caustic soda, contains various impurities, some of which interfere, to a certain extent, with the rigid accuracy of the analytical processes here described, the principal are sulphide and hyposulphite of sodium. As, however, the greater proportion of alkali made by English manufacturers is contaminated to a slight extent only with these impurities, they may, for most technical purposes, be disregarded. The best methods of estimating them are described § 35.

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POTASH.

§ 14. A PORTION of pure carbonate of potash, tested and found to be free from sulphates and chlorides, was ignited in a platinum crucible, cooled under the exsiccator, and quickly weighed, the weight was 3.467 Gm. It was dissolved and 60 CC of normal oxalic acid added from the burette, heated to expel all carbonic acid, and titrated backward with normal alkali, of which 9.9 CC were required, leaving 50.1 CC as the exact quantity of acid. By referring to the table for carbonate of potash, it is found that—

$$50 \text{ CC} = 3.4555 \text{ Gm.}$$

$$0.1 \text{ CC} = .0069 \text{ „}$$

$$\text{Total } 3.4624 \text{ Gm.}$$

Instead of 3.467 Gm., the difference is barely 5 milligrammes.

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**MIXTURES OF CAUSTIC WITH CARBONATED ALKALIES.**

§ 15. THE alkaline salts of commerce, and also alkaline lyes used in soap, paper, starch, and other manufactories, consist generally of a mixture of caustic and carbonated alkali. If it be desired to ascertain the proportion in which these mixtures occur, the total alkaline power of a weighed or measured quantity of substance is obtained and noted, a like quantity is then brought into solution to about 150 CC, in a 300 CC flask, heated to boiling, and enough solution of chloride of barium added, to remove all the carbonic acid from the soda or potash, there must be an excess of chloride, but as it does not interfere with the accuracy of the result the exact quantity is of no consequence.

The flask is now filled up to the 300 CC mark with distilled water, corked and put aside to settle. When the supernatant liquid is clear, take out 100 CC with a pipette and titrate with normal nitric acid to the neutral point. The number of CC multiplied by 3, will be the quantity of acid required for the caustic alkali in the original weight of substance, because only  $\frac{1}{3}$  was taken for analysis.

The precipitated carbonate of baryta may be thrown upon a filter, washed well with hot water, and titrated with normal nitric acid, as described further on, if the operator chooses, instead of the original analysis for the total alkalinity, or both plans may be adopted as a check upon each other.

The principle of this method is, that when chloride of barium is added to a mixture of caustic and carbonated alkali, the carbonic acid of the latter is precipitated as an equivalent of carbonate of baryta, while the equivalent proportion of caustic alkali remains in solution as hydrate of baryta. By multiplying the number of CC of acid required to saturate this free alkali with the atomic weight of either caustic potash or soda, according to circumstances, the quantity of substance originally present in this state will be obtained.

As caustic baryta absorbs carbonic acid very readily when exposed to the atmosphere, it is preferable to allow the precipitate of carbonate of baryta to settle in the flask as here described, rather than to filter the solution as recommended by some operators.

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AMMONIA, FREE AND COMBINED.

§ 16. In estimating the strength of solutions of ammonia by the alkalimetric method, it is better to avoid the tedious process of weighing any exact quantity, and to substitute for it the following plan, which is applicable to most liquids for the purpose of ascertaining both their absolute and specific weights.

Let a small and accurately tared flask, beaker, or other convenient vessel be placed upon the balance, and into it 10 CC of the ammoniacal solution delivered from a very accurately graduated 10 CC pipette. The weight found is, of course, the absolute weight of the liquid in grammes; suppose it to be 9.65 Gm., move the decimal point one place to the left, and the specific weight or gravity is at once given, (water being 1) which in this case is .965.

The 10 CC weighing 9.65 Gm., was now titrated with normal acid, of which 49 CC were required, therefore  $49 \times .017 = .833$  Gm.  $\text{NH}_3 = 8.64$  per cent. of real ammonia; according to Otto's table 9.65 spec. grav., is equal to 8.50 per cent. Carbonate of ammonia and a mixture of the same with bicarbonate, as it most commonly occurs in commerce, may be titrated direct with normal acid for the percentage of real ammonia. The carbonic acid can be determined by precipitation hot with chloride of barium, and when the precipitate is well washed, dissolving it with an excess of normal acid and titrating backward with normal alkali, as described more fully under the head

of alkaline earths, the number of CC of acid used multiplied by 0.022 (the equiv. of  $\text{CO}_2$ ) will give the weight of carbonic acid present in the sample.

Instead of the 10 CC, a 100 grm. or 10 dm. pipette can be used for taking specific gravity, in which case the decimal point is moved two places to the left, grain weights being of course used in the weighing.

It must be borne in mind that this system can only be used properly with tolerably delicate balances and very accurate pipettes. The latter should invariably be tested by taking the spec. grav. of distilled water at 60 Fahr., according to the plan described.

The ammonia contained in rain or other waters can be estimated according to Boussingault's researches, by distilling off about one-third of the water under examination, with the addition of a little caustic potash or quicklime, the exact measures, both of the distillate and the original water being known, the former may be titrated with normal acid, and the quantity of ammonia in the original specimen at once ascertained by a slight calculation; generally speaking, not less than a couple of litres or 30,000 grains should be used for the examination.

If the ammoniacal liquor of gas works is examined in this way, less than the quantities mentioned above will of course suffice, but in such cases the operator must use his own judgment. The direct estimation of ammonia, in its neutral salts by distillation, is best effected in the apparatus shewn in Fig. 11. The little flask, holding about 200 CC and placed upon the wine gauze, contains the ammoniacal substance. The tube *d* is filled with strong solution of caustic potash or soda; the large flask holds about a pint, and contains a measured quantity of normal acid, part being contained in the tube *c*, which is filled with broken glass, and through which the normal acid has been poured.

The substance to be examined is weighed and put into the distilling flask with a little water, the apparatus then being

made tight at every part, some of the caustic alkali is allowed to flow in by opening the clip, and the spirit lamp is lighted under it.

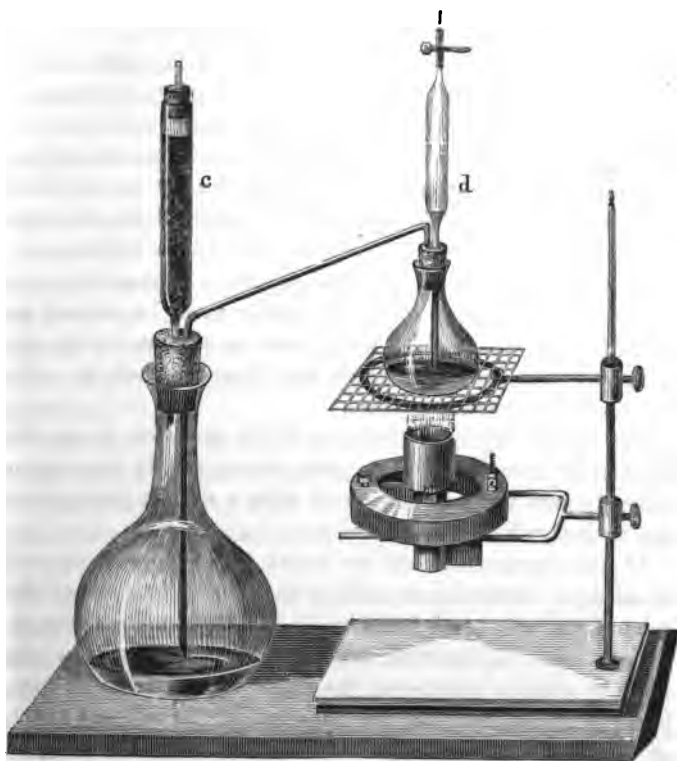


Fig. 11.

The contents are brought to gentle boiling, taking care that the froth if any does not enter the distilling tube. It is well to use a common spirit lamp held under the flask in the hand; in case there is any tendency to boil over the lamp can be removed immediately and the flask blown upon by the breath, which brings down the temperature in a moment. In examining guano and other substances containing organic matter by



this means, the tendency to frothing is considerable, and unless the above precautions are taken the accuracy of the results will be interfered with.

The distilling tube has both ends cut slantwise, and the lower end just reaches to the surface of the acid, to which a little litmus is added. The quantity of acid used must, of course, be more than sufficient to combine with the ammonia produced; the excess is afterwards ascertained by titration with normal alkali.

It is advisable to continue the boiling for say ten or fifteen minutes, then rest for the same time to allow all the ammonia to be absorbed. Lastly, boil once or twice for a minute or so, take away the lamp, and allow the apparatus to stand about an hour before being opened. The tube *c* must be washed out into the flask with distilled water, so as to carry down the acid with any combined gas which may have reached it. The titration then proceeds as usual.

The results are very satisfactory if the operation is carefully conducted; instead of the foregoing direct plan, in the case of tolerably pure neutral ammoniacal salts, a simpler indirect one can be used, which is as follows:—

If the ammoniacal salt be boiled in an open flask with solution of carbonate of soda, potash, or caustic alkali, the ammonia is entirely set free, leaving its acid combined with the fixed alkali. If, therefore, the strength and quantity of the alkaline solution are known, the excess beyond that, necessary to supplant the ammonia, can be found by the ordinary system of titration. The boiling of the mixture must be continued till a piece of red litmus paper, held in the steam from the flask, is no longer turned blue.

Example, 1.5 Gm. of purest sublimed chloride of ammonium was brought into a flask with 40 CC of normal carbonate of soda, and boiled till all ammonia was expelled, then titrated backward with normal sulphuric acid, of which 11.9 CC were required; this left 28.1 CC of normal alkali, which multiplied by .05346 gave 1.502 Gm., instead of 1.5 Gm. originally taken.

**CONVERSION OF NITROGEN IN NITROGENOUS SUBSTANCES INTO  
AMMONIA, AND ESTIMATION BY PELIGOT'S PROCESS.**

§ 17. This process consists in burning a convenient quantity of the dried substance in a combustion tube with soda lime, by which the nitrogen is converted into ammonia, and this latter being led into a measured volume of normal sulphuric acid contained in Will and Varrentrapp's bulb apparatus, combines with its equivalent quantity; the solution is then titrated with standard alkali for the excess of acid, and thus the quantity of ammonia found.

As the combustion tube with its arrangements for organic analysis is well known, and described in any of the standard books on general analysis, it is not necessary to give a description here.

Instead of leading the ammonia through normal acid, hydrochloric acid of unknown strength may be used, evaporated to dryness in a water bath, and the residual chloride of ammonium estimated by either of the processes described above for neutral salts of ammonia.

When it is necessary to estimate very minute portions of ammonia, it is preferable to bring it into the form of chloride, and estimate by decinormal silver solution, as described § 75.

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**ALKALINE EARTHS.**

§ 18. NORMAL nitric acid is the best agent for the titration of the caustic and carbonated alkaline earths, inasmuch as the resulting compounds are all soluble.

In order to obtain a rigidly exact normal acid, it is advisable to graduate it by pure carbonate of lime, either in the form of

the purest Iceland spar, as recommended by Dr. Pincus, or by artificial carbonate, prepared with great care by precipitating pure chloride of calcium with carbonate of ammonia, and boiling the resulting precipitate until it becomes dense; it is then to be washed thoroughly with hot water, dried, ignited gently, and preserved in bottles closed with a chloride of calcium tube.

By means of either of these forms of carbonate of lime, it is possible at any time to titrate a dilute nitric acid, so as to bring it to the normal state, but as more acid must be used for the decomposition than is actually required to saturate the lime and expel the carbonic acid, the excess must be estimated by the help of normal alkali.

I somewhat question whether the complication introduced by this method, is more exact in its results than by titrating the nitric acid direct by means of carbonate of soda. If the very purest carbonate of soda is used, and every precaution taken in igniting and weighing it, there cannot be much scope for error, nevertheless it is desirable to check the results in every possible way, and as pure carbonate of lime is not difficult to obtain, and does not contract moisture like carbonate of soda, it is a reliable basis upon which to work.

The nitric acid used should be colourless, free from chlorine and nitrous acid, spec. grav. from 1.35 to 1.4. If coloured from the presence of nitrous or hyponitrous acids, it should be mixed with two volumes of water, and boiled until white. When cold it may be diluted and titrated as above. 1 Gm. of pure Iceland spar in small pieces should require 20 CC of acid, supposing it to be rigidly normal; if slightly stronger or weaker, the exact difference must be found, so that a constant factor may be obtained by which to bring it by calculation to the normal state.

Lime, baryta, and strontian, in the caustic state, or combined with carbonic acid, are dissolved by the aid of heat in an excess of normal acid, and then titrated with normal alkali. Chlorides and nitrates of the same bases are precipitated hot with car-

bonate of ammonia containing caustic ammonia, thoroughly washed with hot water on a filter, and both filter and precipitate, while still moist, pushed through the funnel into a flask, and titrated as above; by deducting the number of CC of alkali from the original quantity of acid used, the proportion of pure base, or its compounds, may be obtained.

## Alkaline Earths.

Substance.	Formula.	Atomic Weight	Quantity to be weighed so that 1 CC or 1 dm. <sup>3</sup> = 1 per cent. of substance.	Normal Factor.
<b>Calcium Ca=40.</b>				
Lime .....	Ca O	28	2.8 Gm., or 28.0 grn.	0.028, or 0.28
Carbonate of Lime	CaO, CO <sub>2</sub>	50	5.0 Gm., or 50.0 grn.	0.05, or 0.50
Sulphate of Lime ... (Gypsum)	CaO, SO <sub>3</sub> + 2H <sub>2</sub> O	86	8.6 Gm., or 86.0 grn.	0.086, or 0.86
<b>Barium Ba=137.</b>				
Caustic Baryta .....	Ba O	76.59	7.659 Gm., or 76.59 grn.	0.07659, or 0.7659
Carbonate of Baryta	Ba O, CO <sub>2</sub>	98.59	9.859 Gm., or 98.59 grn.	0.09859, or 0.9859
Nitrate of Baryta...	Ba O, NO <sub>3</sub>	130.59	13.059 Gm., or 130.59 grn.	0.13059, or 1.3059
Chloride of Barium	Ba Cl	104.05	10.405 Gm., or 104.05 grn.	0.10405, or 1.0405
<b>Strontium Sr=87.</b>				
Strontia .....	Sr O	51.67	5.167 Gm., or 51.67 grn.	0.05167, or 0.5167
Carbonate of Strontia	Sr O, CO <sub>2</sub>	73.67	7.367 Gm., or 73.67 grn.	0.07367, or 0.7367
Chloride of Strontium	Sr Cl	79.13	7.913 Gm., or 79.13 grn.	0.07913, or 0.7913
Nitrate of Strontia	Sr O, NO <sub>3</sub>	105.67	10.567 Gm., or 105.67 grn.	0.10567, or 1.0567

**LIME.**

§ 19. SULPHATE of lime or gypsum may be converted into carbonate by solution in hydrochloric acid, and precipitation by carbonate and caustic ammonia, or fluxed with carbonate of soda, the resulting sulphate of soda washed out, and then titrated as before described. Oxalate of lime is converted into a mixture of caustic and carbonate of lime by ignition.

See also §§ 39, 60.

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**BARYTA.**

§ 20. MOHR recommends that after the measured volume of normal acid is added to the caustic baryta or its carbonate, and the decomposition complete, enough pure neutral sulphate of soda should be added to precipitate the baryta as sulphate, then to proceed with the titration for the excess of acid as usual, the precipitated sulphate of baryta does not interfere with the visible ending of the reaction, while it prevents the difficulty which might arise from the partially insoluble nitrate of baryta.

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**STRONTIAN.**

§ 21. THE compounds of strontian are determined precisely as lime and baryta.

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**CARBONIC ACID.****as in Combination.**

§ 22. It will be readily seen, from the foregoing article on alkaline earths, that carbonic acid, in combination with a great variety of bases, can be estimated by the volumetric method with a high degree of accuracy.

The carbonic acid to be estimated may be brought into combination with either lime or baryta, these bases admitting of the firmest combination as neutral carbonates.

If the carbonic acid exists in a soluble form as a monocarbonate of alkali, the decomposition is effected by the addition of chlorides of barium or calcium, as before directed; if as bicarbonate or a compound between the two, ammonia must be added with either of the chlorides.

As solution of ammonia most frequently contains carbonic acid, it must be removed by the aid of chloride of barium or calcium previous to use, should there be any present. It may be kept from absorbing carbonic acid by means of the tube described for normal alkali.

Example, 1 Gm. of pure anhydrous carbonate of soda was dissolved in water, precipitated hot with chloride of barium, filtered and washed thoroughly with boiling water, the filter and precipitate were then brought into a flask, and 26 CC of normal nitric acid added, then titrated with normal alkali, of which 7.2 CC were required, = 18.8 CC of acid, this multiplied by .022 (1 CC acid = .022  $\text{CO}_2$ ) gave .4136 Gm.  $\text{CO}_2$  = 41.36 per cent., or multiplied by .053 gave .9964 Gm. carbonate of soda instead of 1 Gm.

1 Gm. of pure and dry bicarbonate of soda in powder was dissolved and precipitated with ammonia and chloride of calcium, the precipitate washed with boiling water till all ammonia was removed, the precipitate and filter then titrated with normal acid and alkali—the quantity of acid used was 23.5 CC = 51.7 per cent. of  $\text{CO}_2$ —the percentage, supposing the salt to be absolutely pure, would be 52.3.

There seems to be no difference, with respect to accuracy, between chloride of calcium or barium as the precipitant; but as the carbonate of lime can be more readily washed without clogging the filter, it is preferable to use the chloride of calcium.

It sometimes occurs that substances have to be examined for

carbonic acid, which do not admit of being treated as above described; such for instance as the carbonates of the metallic oxides, (white lead, calamine, etc.) carbonates of magnesia, iron, and copper, the estimation of carbonic acid in cements, mortar, and many other substances. In these cases the carbonic acid must be evolved from the combination by means of a stronger acid, and conducted into an absorption apparatus containing ammonia, then precipitated with chloride of barium or calcium and titrated as before described. The following form of apparatus (Fig. 12) has afforded Mohr the most satisfactory results.



Fig. 12.

It is the same arrangement in principle as shown in Fig. 11, for the distillation of ammonia, with the exception that the flask *b* and tube *d* are somewhat larger and are placed on a level with the larger flask.

The weighed substance from which the carbonic acid is to be evolved, is brought into *b* with a little water and litmus, the tube *d* contains strong hydrochloric acid, and *c*, broken glass wetted with ammonia free from carbonic acid. (It should be heated with a little chloride of calcium in a test tube; if pure, it will remain clear.) The flask *a* is about  $\frac{1}{2}$  filled with the same ammonia, the bent tube must not enter the liquid. When all is ready and the corks tight, (best secured by wetting them,) warm the flask *a* gently so as to fill it with vapour of ammonia, then open the clip and allow the acid to flow circumspectly upon the material, which may be heated until all carbonic acid is apparently driven off, then by boiling and shaking the last traces can be evolved and the operation ended. When cold, the apparatus may be opened, the end of the bent tube washed into *a*, and also a good quantity of boiled distilled water passed through *c*, so as to carry down any carbonate of ammonia that may have formed. Then add solution of chloride of calcium boil, filter, and titrate the precipitate, as before described.

During the filtration and while ammonia is present there is a great avidity for carbonic acid, therefore boiling water should be used for washing, and the funnel kept covered with a small glass plate.

#### Free Carbonic Acid Gas.

Well or spring water, and also all mineral waters containing free carbonic acid, can be examined by collecting measured quantities of them at their source, in bottles containing a mixture of chloride of calcium and ammonium, afterwards boiling the mixture and titrating the precipitate as usual.



The following is the best method to be pursued for ordinary drinking waters not containing large quantities of carbonic acid. 500 CC of the water are put into a flask with a measured quantity of weak baryta water, the strength of which is previously ascertained by means of *decinormal* nitric acid, then boiled, well corked, and put aside to cool and settle; when cold and the precipitate subsided, take out 300 CC of the clear liquid with a pipette, or pour it off without disturbing the sediment. Let this be titrated with decinormal nitric acid; the quantity required must be calculated for the total water and baryta solution, there being 300 CC only taken; the number of CC so found must be deducted from the original quantity required for the baryta solution added; the remainder multiplied by  $\cdot 0022$ . (the acid being decinormal) will give the weight of carbonic acid in the 500 CC, free and as bicarbonate.

By collecting the precipitate and titrating it as previously described, the total carbonic acid may be found.

Example, 500 CC spring water were mixed with 30 CC baryta water = 54.5 CC decinormal nitric acid, boiled, corked, and set aside to cool; 300 CC of the clear liquid titrated with decinormal acid, of which 6.5 CC were required, consequently the 530 CC required 11.5 CC; this deducted from 54.5 CC, the quantity required for the 30 CC baryta solution, leaves 43 CC  $\frac{N}{10}$  acid, which multiplied by  $\cdot 0022$ , gives  $\cdot 0946$  Gm.  $\text{CO}_2$  in the 500 CC of water, free and as bicarbonate.

The precipitate required 8.4 CC normal nitric acid =  $\cdot 1848$  Gm.  $\text{CO}_2$ , which is the total weight combined and free; consequently the following calculation will give the results in detail.

Total $\text{CO}_2$ .....	$\cdot 1848$ Gm.
Deduct free and as bicarbonate	$\cdot 0946$ „
Leaving combined ...	$\cdot 0902$ „

The weight of  $\text{CO}_2$ , as bicarbonate, will, of course be equal to

this, and the two = .1804 Gm., which deducted from 1848 Gm., gives—

Free CO <sub>2</sub> .....	.0044 Gm.
Ditto as bicarbonate .....	.0902 „
Ditto as neutral carbonate .....	.0902 „
Total.....	.1848 „ CO <sub>2</sub>

If the water contains magnesia, some solution of chloride of ammonium must be added to prevent its precipitation by the baryta; and instead of boiling, which would decompose and dissipate the ammonia, the flask should be closely stoppered and digested in hot water; when perfectly cold and clear the examination may be completed as above. If it be desirable to ascertain the volume of carbonic acid from the weight, 1000 CC of gas, at 32° and 30<sup>in</sup>. bar, weigh 1.96663 Gm. 100 cubic inches weigh 47.26 grains.

For ascertaining the quantity of carbonic acid in bottled aerated waters, such as soda, seltzer, potass, and others, the following apparatus is useful. Fig. 13 is a brass tube made like a



Fig. 13.



Fig. 14.

corkborer about 5 inches long, having 4 small holes, two on each side, at about 2 inches from its cutting end, the upper end is securely connected with the bent tube from the absorption flask (Fig. 14,) by means of a vulcanized tube; the flask con-

tains a tolerable quantity of pure ammonia into which the delivery tube dips: the tube *a* contains broken glass moistened with ammonia.

Everything being ready the brass tube is greased with tallow or paraffin, and the bottle being held in the right hand, the tube is screwed a little aslant through the cork, by turning the bottle round, until the holes appear below the cork and the gas escapes into the flask; when all visible action has ceased, after the bottle has been well shaken two or three times to evolve all the gas that can be possibly eliminated, the vessels are quietly disconnected, the tube *a* washed out into the flask, and the contents of the bottle added also, the whole is then precipitated with chloride of calcium and boiled, and the precipitate titrated as usual. This gives the total carbonic acid free and combined.

To find the quantity of the latter, another bottle of the same manufacture must be evaporated to dryness, and the residue gently ignited, then titrated with normal acid and alkali; the amount of carbonic acid in the monocarbonate deducted from the total will give the weight of gas originally present.

The volume may be found as follows:—1000 CC of carbonic acid at 32° Fahr., weigh 1.966 Gm. Suppose, therefore, that the total weight of carbonic acid found in a bottle of ordinary soda water was 2.8 Gm. and the weight combined with alkali .42 Gm., this leaves 2.38 Gm. CO<sub>2</sub> in a free state—

$$1.966 : 2.38 :: 1000 : x = 1210 \text{ CC.}$$

If the number of CC of carbonic acid found is divided by the number of CC of soda water contained in the bottle examined, the quotient will be the volume of gas compared with that of the soda water. In this case, the contents of the bottle were ascertained by marking the height of the fluid previous to making the experiment; the bottle was afterward filled to the same mark with water, emptied into a graduated cylinder, and found to measure 292 CC, therefore

$$\frac{1210}{292} = 4.14 \text{ vols. CO}_2$$

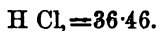
**ACIDIMETRY.**

§ 23. EITHER pure potash or soda, or their carbonates or ammonia, may be used for standard solutions in acidimetry, just as have been described for alkalimetry.

If it be desired to use the pure alkaline solutions the bottles in which they are preserved, and also the burettes in which they are used, must be closed with a carbonic acid tube. The manipulation is in all cases the same as in the estimation of alkalies.

It is well to bear in mind that the neutral salts produced by some acids and alkalies have a decided alkaline reaction on litmus, these are mostly salts of the weak organic acids, such as acetic, tartaric, and citric, but the actual errors occurring in the analysis of these substances by a practised hand are very slight and may in most cases be quite disregarded.

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**HYDROCHLORIC ACID.**

§ 24. THE specific gravity is taken just as described for ammonia, namely—with an accurately graduated pipette; if 10 CC are taken, the resulting weight is the spec. grav., when the decimal point is moved one place to the left. If 5 CC are taken, the weight in grammes must be divided by 5, the quotient will be the spec. grav.

Example, 5 CC of white and tolerably pure acid was put into a small tared bottle and the weight found to be 5.6 Gm., this divided by 5 gave the spec. grav. as 1.12. It was diluted and titrated with normal alkali, of which 37.1 CC were required, this multiplied by .03646 gave 1.3526 Gm. = 24.2%. Ure's table gives 24.46 for the same spec. grav.

In order to ascertain the percentage of hydrochloric acid gas in any sample, it is only necessary to multiply the weight of gas found by normal alkali by 100, and divide by the weight of acid originally taken for analysis, the quotient will be the percentage. Or, simpler than this, if the  $\frac{1}{10}$  atom in grammes, 3.646 Gm., or 1 atom in grains, = 36.46 gra., be weighed, the number of CC or decems will be the percentage respectively.

#### NITRIC ACID.

$$\text{NO}_x = 54.$$

§ 25. 5 CC of pure nitric acid weighed 6.07 Gm., the spec. grav. was, therefore, 1.215—the quantity of normal alkali required was 33 CC, which multiplied by .054 gave 1.782 Gm.  $\text{NO}_x = 29.3\%$ ; Ure's table gives 29.5% for the same specific gravity.

#### NITRIC ACID IN COMBINATION.

##### Factors.

Normal acid	×	0.054	= $\text{NO}_x$
Ditto	×	0.10111	= $\text{KO}, \text{NO}_x$
Metallic iron	×	0.32143	= $\text{NO}_x$
Double iron salt	×	0.0459	= $\text{NO}_x$
Metallic tin	×	0.1144	= $\text{NO}_x$

§ 26. THE accurate estimation of nitric acid in combination presents great difficulties and can only be secured by indirect means, it is hoped, however, that the methods here given are sufficient for most purposes, very few of them can be said to be simple, but it is to be feared that no simple process can ever be obtained for the determination of nitric acid in many of its combinations.

**1. Gay Lussac's method modified by Abel, (applicable only to Alkaline Nitrates.)**

This process depends upon the conversion of nitrates of soda or potash into carbonates by ignition with carbon, and the titration of the carbonate so obtained, by normal sulphuric or oxalic acid, as described in alkalimetry. The number of CC or dm. of normal acid required multiplied by 0.10111 or 1.0111, will give the weight of pure nitrate of potash in grammes or grains; by 0.085 or 0.85, the weight of nitrate of soda in grammes or grains.

The best method of procedure is as follows:—The sample is finely powdered and dried in an air bath, and 1 gramme, or an equivalent quantity in grains, weighed, introduced into a platinum crucible, and mixed with a fourth of its weight of pure graphite, (prepared by Brodie's process,) and four times its weight of pure ignited chloride of sodium. The crucible is then covered and heated moderately for twenty minutes over a Bunsen's burner, or for eight or ten minutes in a muffle, (the heat must not be so great as to volatilize the chloride of sodium to any extent.) If sulphates are present they will be reduced to sulphides; and as these would consume the normal acid and so lead to false results, it is necessary to sprinkle the fused mass with a little powdered chlorate of potash, and heat again moderately till all effervescence has ceased. The crucible is then set aside to cool, warm water added, the contents brought upon a filter, and washed with hot water till the washings are no longer alkaline. The filtrate is then titrated with litmus and normal acid in the ordinary way, or better by the residual method described in alkalimetry.

**2. Acidimetric Method.**

The principle of this mode of determinating nitric acid is described in § 34, but is only applicable where the base

is precipitable by pure or carbonated alkalies, and where no other acid is present, having a precipitable base ; with nitrates of metallic oxides and alkaline earths, very accurate results are obtained.

### 3. Estimation of Nitrates by Distillation with Sulphuric Acid.

This method is of very general application, but particularly so with the impure alkaline nitrates of commerce, the process, however, needs careful manipulation, but yields accurate results.

There are two methods of procedure.

a. To bring the weighed nitrate into a small tubulated retort with a cooled mixture of water and strong sulphuric acid, in the proportion of 10 CC water and 5 CC sulphuric acid for 1 Gm. of nitrate ; the neck of the retort is drawn out to a point and bent downward, entering a potash or other convenient bulb apparatus containing normal caustic alkali ; the retort is then buried to its neck in the sand bath, and heated to 170°C, (338° Fahr.) so long as any liquid distils over ; the heat must never exceed 175°C (347° Fahr.) otherwise traces of sulphuric acid will come over with the nitric acid. The quantity of acid distilled over, is found by titrating the fluid in the receiver with normal acid, as usual.

b. Distillation in a Partial Vacuum, (Finkener.) By this arrangement there is no danger of contaminating the distillate with sulphuric acid, inasmuch as the operation is conducted in a water bath, and when once set going needs no superintendence.

The retort is the same as before described, but the neck is not drawn out or bent ; the stopper of the tubulure must be well ground. The receiver is a 200 CC flask with narrow neck, containing the requisite quantity of normal alkali diluted to about 30 CC. The receiver is bound, air tight, with the neck of the retort, (which should reach nearly to the middle of the

flask) by means of a vulcanized tube: the proportions of acid and water before-mentioned, are brought into the retort with a tube funnel. The stopper of the retort is then removed and the contents, both of the receiver and retort, heated by spirit or gas lamps to boiling, so as to drive out the air, the weighed nitrate contained in a small tube is then dropped into the retort, the stopper inserted, the lamps removed, and the retort brought into the water bath, while the receiver is kept cool with wet tow or placed in cold water. The distillate is titrated as before, 1 or 2 Gm. saltpetre, require about four hours for the completion of the process. According to H. Rose, (*Zeitschrift für an. Chem.* Part iii, page 311,) Finkener obtained very accurate results by this method.

When chlorides are present in the nitrate a small quantity of moist oxide of silver is added to the mixture before distillation.

**4. Estimation by conversion into Ammonia. (Schulze and Vernon Harcourt.)**

The principle of this method, which gives very satisfactory results, is based on the fact that when nitric acid is heated with a strong alkaline solution and zinc added, ammonia is evolved; when zinc alone is used, however, the quantity of ammonia liberated is not a constant measure of the nitric acid present. Schulze found that when the zinc was platinized, or when sodium or aluminium amalgam was used, the reaction was perfect.—(*Chem. Centr. blatt*, 1861, pp. 657 and 833.) Vernon Harcourt appears to have arrived independently at the same result, by using a mixture of iron and zinc.—(*Journal of Chem. Soc.*, 1862, p. 381).

As the latter process seems, on many accounts, preferable to that of Schulze, a short description of the apparatus, etc., devised by Harcourt is given.

The distilling flask holds about 200 CC, and is closely connected, by a bent tube, with another smaller flask in such a



manner that both may be placed obliquely upon a sand bath, the bulb of the smaller flask coming just under the neck of the larger. The oblique direction prevents the spirting of the boiling liquids from entering the exit tubes, but as a further precaution, these latter are in both flasks turned into the form of a hook; from the second flask, which must be somewhat wide in the mouth, a long tube passes through a Liebig's condenser, (which may be made of wide glass tube,) into an ordinary tubulated receiver, containing normal sulphuric acid coloured with litmus, the end of the distilling tube reaches to about the middle of the receiver, through the tubulure of which Harcourt passes a bulb apparatus of peculiar form, containing also coloured normal acid; instead of this latter, however, a chloride of calcium tube, filled with broken glass and moistened with the acid as in Fig. 11, will answer the purpose; the distilling tube should be cut at about two inches from the cork of the second flask, and connected by means of a good fitting vulcanized tube; by this means water may be passed through the tube when the distillation is over, so as to remove any traces of ammonia which may be retained on its sides; all the corks of the apparatus should be soaked in hot paraffin so as to fill up the pores.

All being ready, about 50 Gm. of finely granulated zinc\* (best made by pouring molten zinc into a warm iron mortar while the pestle is rapidly being rubbed round) is put into the larger flask with about half the quantity of clean iron filings which have been ignited in a covered crucible; the weighed nitrate is then introduced, either in solution or with water in sufficient quantity to dissolve it, strong solution of caustic potash added, and the flask immediately connected with the apparatus, and placed on a small sandbath heated by a gas-burner, a little water is previously put into the second flask. Convenient proportions of material are  $\frac{1}{2}$  Gm. nitre and about 20 CC each of water, and solutions of potash spec. grav. 1.3.

\* After the distillation is over, the zinc and iron may be well washed, then dried, and preserved for the next operation.

Heat is now applied to that part of the sandbath immediately beneath the larger flask, and the mixture is gradually raised to the boiling point; when distillation has actually commenced, the water in the second flask is made to boil gently; by this arrangement the fluid is twice distilled, and any traces of fixed alkali which may escape the first, are sure to be retained in the second flask. The distillation with the quantities above named will occupy about an hour and a half, and is completed when hydrogen is pretty freely liberated as the potash becomes concentrated. The lamp is then removed and the whole allowed to cool, the distilling tube rinsed into the receiver, also the tube containing broken glass, the contents of the receiver are then titrated with normal caustic potash or soda as usual.

Chlorides and sulphates do not interfere with the accuracy of the results.

A mean of several experiments with pure nitre gave 52.83 % of nitric acid instead of 53.41 %/. The process does not give such accurate results with some metallic nitrates.

#### 5. Pelouze's Method.

The principle upon which this well known process is based is as follows:

*a.* When nitric acid ( $\text{NO}_3$ ) in the form of a nitrate, is brought in contact with a solution of protoxide of iron, mixed with free hydrochloric acid, and heated, 3 eq. of the oxygen contained in the nitric acid pass over to the iron, forming a persalt, while the base combines with hydrochloric acid, and nitric oxide ( $\text{NO}$ ) is set free; 6 eq. of iron=168 are oxidized by 1 eq. nitric acid=54 ( $6 \text{ Fe O} + \text{NO}_3 = 3 \text{ Fe}_2 \text{ O}_3 + \text{NO}$ ). If, therefore, a weighed quantity of the nitrate be mixed with an acid solution of protochloride or protosulphate of iron, of known strength, in excess, and the solution boiled, to expel the liberated nitric oxide, then the amount of unoxidized iron remaining in the mixture, found

by a suitable method of titration, the quantity of iron converted from protoxide into peroxide, will be the measure of the original nitric acid in the proportion of 168 to 54, or by dividing 54 by 168 the factor 0.32143 is obtained, so that if the amount of iron changed as described be multiplied by this factor, the product will be the amount of nitric acid.

This method, though theoretically perfect, is in practice liable to serious errors, owing to the readiness with which a solution of protoxide of iron absorbs oxygen from the atmosphere. On this account accurate results are only obtained by conducting hydrogen or carbonic acid gas through the apparatus while the boiling is carried on. This modification has been adopted by Fresenius with very satisfactory results. The boiling vessel may consist of a small tubulated retort, supported in such a manner that its neck inclines upward, a cork is fitted into the tubulure, and through it is passed a small tube connected with a vessel for generating either carbonic acid or hydrogen. If a weighed quantity of pure metallic iron is used for preparing the solution, the washed carbonic acid or hydrogen should be passed through while it is being dissolved; the solution so obtained, or one of double sulphate of iron and ammonia, (§ 43, 1,) of known strength being already in the retort, the nitrate is carefully introduced, and the mixture heated gently by a small lamp, or by the water bath, for ten minutes or so, then boiled until the dark red colour of the liquid disappears, and gives place to the brownish yellow of perchloride of iron; the retort is then suffered to cool, the circulation of carbonic acid or hydrogen still being kept up, then the liquid diluted freely and titrated with permanganate of potash, as in § 43. Owing to the irregularities attending the use of permanganate with hydrochloric acid, it is preferable to dilute the solution less, and titrate with bichromate of potash, as in § 44. 2 Gm. pure iron, or its equivalent in double iron salt,  $\frac{1}{2}$  Gm. saltpetre and about 60 CC strong hydrochloric acid, are convenient proportions for the analysis.

b. Direct titration of the resulting perchloride of iron. This modification of Pelouze's original method was suggested by Braun, (*Journ. f. pract. Chem.*, 81, 421,) and is decidedly better in principle than the residual titration of the protochloride of iron by permanganate. Braun, however, estimates the peroxide by adding an excess of iodide of potassium, digesting for a time at a gentle heat, then titrating the resulting free iodine by hyposulphite of soda. 3 eq. of iodine so found corresponding to 1 eq. nitric acid; the disadvantage possessed by this plan is that variable quantities of water or hydrochloric acid seriously affect the accuracy of the results. Fresenius has therefore suggested the use of protochloride of tin for titrating the peroxide of iron, with the best results, (*Zeitschrift f. an. Chem.*, part 1, p. 34.) For the details of the process see § 50.

The following plan of procedure is recommended as the best by the same authority.

A solution of protosulphate of iron is prepared] by dissolving 100 Gm. of the crystals in 500 CC of hydrochloric acid of spec. grav. 1.10; when used for the analysis, the small proportion of peroxide of iron invariably present in it is found by titrating with protochloride of tin, as in § 50. The nitrate being weighed or measured, as the case may be, is brought together with 50 CC (more or less, according to the quantity of nitrate) of the iron solution into a long necked flask, through the cork of which two glass tubes are passed, one connected with a carbonic acid apparatus, and reaching to the middle of the flask, the other simply an outlet for the passage of the gas. When the gas has driven out all the air, the flask is at first gently heated, and eventually boiled, to dispel all the nitric oxide. The carbonic acid tube is then rinsed into the flask, and the liquid, while still boiling hot, titrated for perchloride of iron, as in § 50. The liquid must, however, be suffered to cool before titrating with iodine for the excess of protochloride of tin. While cooling, the stream of carbonic acid should still be continued. The

quantity of iron changed into peroxide, multiplied by the factor 0.32143, will give the amount of nitric acid. Example:

*a.* A solution of protochloride of tin was used for titrating 10 CC of solution of pure perchloride of iron, containing 0.215075 Gm. iron. 25.65 CC of tin solution were required, therefore that quantity was equal to 0.069131 Gm.  $\text{NO}_3$ .

*b.* 50 CC of acid solution of protosulphate of iron was titrated with tin solution for peroxide, and 0.24 CC were required.

*c.* 1 CC tin solution = 3.3 CC iodine solution.

*d.* 0.2177 Gm. of pure nitre was boiled, as described, with 50 CC of the acid protosulphate of iron, and required respectively 45.03 CC tin solution, and 4.7 CC iodine—

$$\begin{array}{rcl} 4.7 \text{ iodine solution} & = & 1.42 \text{ Sn. Cl.} \\ \text{The peroxide in the protosulphate solution} & = & 0.24 \text{ ,,} \\ & & 1.66 \end{array}$$

$45.03 - 1.66 = 43.37$ , therefore  $25.65 : 0.069131 = 43.37 : x$ ,  $x = 0.1169 \text{ NO}_3$ , instead of 0.1163, or 53.69 % instead of 53.41. A mean of this, with three other estimations, using variable proportions of tin and iron solutions, gave exactly 53.41 %. The process is therefore, though troublesome, entirely satisfactory.

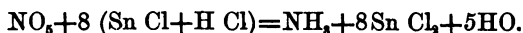
#### 6. Schlösing's Method.

The solution of nitrate is boiled in a flask till all air is expelled, then an acid solution of protochloride of iron drawn in, the mixture boiled, and the nitric oxide gas collected over mercury in a balloon filled with mercury and milk of lime, the gas is then brought, without loss, in contact with oxygen and water, so as to convert it again into nitric acid, then titrated with normal alkali as usual.

This method was devised by Schlösing for the estimation of nitric acid in tobacco, and is especially suitable for that and similar purposes, where the presence of organic matter would interfere with the direct titration of the iron solution. Where the quantity of nitric acid is not below 0.15 Gm., the process is very accurate, but needs a special and rather complicated arrangement of apparatus, the description of which may be found either in the author's original paper, "Annal. de Chim.," 3 sér, tom. 40, 479, or "Journ. für pract. Chem.," 62, 142, also abridged in "Fresenius' Quantitative Analysis," fourth German, or second English edition. The process is less troublesome in practice than is generally supposed.

**7. Estimation by conversion into Ammonia with Chloride of Tin,  
(Pugh.)**

This process is based on the fact that when a nitrate is digested under pressure, and at a temperature of about 320° Fahr. (160° C) with an excess of protochloride of tin and hydrochloric acid, the following reaction occurs :



1 eq. of nitric acid, therefore, under the above conditions, converts 8 eq. of tin from the state of proto to perchloride, consequently, if an unknown quantity of nitric acid be digested with a sufficient excess of solution of protochloride of tin of known strength, and the quantity changed into perchloride be afterward found by a suitable method of titration, the proportion of nitric acid will be found, supposing in all cases that no other substance is present, capable of affecting the same change in the tin solution.

Pugh arrived at the knowledge of the reaction described, by careful experiments, which are detailed in the Quarterly Journal of the Chemical Society, (vol. xii, part 1, page 35,) and used the process devised by Streng for titrating the strength of the

tin solution, namely, bichromate of potash, iodide of potassium, and starch. Experience has shewn, however, that the estimation of tin by this method is far from satisfactory, owing to the variable amount of oxidation which the tin solution undergoes when different quantities of water or acid are present during the titration.

In my experiments on the process, I have therefore adopted the method of Lenssen (§ 57, 1) for estimating the strength of the tin solution, with the most satisfactory results, using in all cases an accurately weighed quantity of pure nitrate of potash for the analysis. One example in detail will make the process clear.

a. A solution of pure nitre was prepared so that 1 CC= $0.1$  Gm.  $\text{KO},\text{NO}_3$ .

b. A solution of pure tin was made by putting a quantity of the granulated metal into a large platinum capsule, and pouring over it a good quantity of strong hydrochloric acid; when the action, assisted by a gentle heat, had somewhat slackened, the liquid was decanted into a well-stoppered bottle, about a third of its quantity of strong and pure hydrochloric acid added, and the bottle set aside for future use.

c. A piece of stout combustion tube, about half an inch diameter and fifteen inches long, was closed at one end, then heated before the blowpipe at about nine inches from the closed end, and drawn out for the space of an inch to a narrow neck; the tube was then cut off just above this neck, so as to leave a kind of funnel mouth.

d. 1 CC of the tin solution was measured with a very accurate pipette into a good sized flask; about 3 or 4 CC of saturated solution of tartrate of soda and potass added; then a solution of pure carbonate of soda, till all effervescence was over, and the liquid clear and slightly alkaline; the sides of the flask were then washed down with cold distilled water, and about 20 CC of saturated solution of bicarbonate of soda delivered in; then starch liquor, and  $\frac{N}{10}$  iodine solution from a  $\frac{1}{10}$  CC burette,

till the blue colour appeared. 17.9 CC were required, and as 1 CC of  $\frac{N}{10}$  iodine corresponds to 0.0059 tin, 1 CC of the tin solution contained 0.10561 Gm. tin.

a. 2 CC of the solution *a* were then measured into the tube *c*. 14 CC of tin solution added, the funnel neck washed down with a few drops of water, a fragment of pure marble dropped in to produce carbonic acid, and thus dispel all air from the tube, when the evolution of gas had ceased, the neck was heated and well closed; about two inches of space was thus left filled with carbonic acid. When the closed end was cooled, the tube was shaken so as to mix the liquids well, put into a copper air bath, and heated up to 320° Fahr. (160° C.) for about fifteen minutes; then allowed to cool, and when perfectly cold the end of the tube broken off, the contents transferred to a large flask, and treated with tartrate of soda and potash, and carbonate of soda, as in *d*; the tube was then washed through with cold distilled water into the flask, bicarbonate of soda, in solution or in powder, added, and the unchanged tin solution titrated with  $\frac{N}{10}$  iodine, as described in *d*, the quantity required was 88.6 CC. The calculation was therefore as follows.

1 CC tin solution = 0.10561 Gm. tin, consequently 14 CC = 1.47854 Gm., from this must be deducted the weight of tin corresponding to 88.6 CC  $\frac{N}{10}$  iodine = 0.52274 Gm., shewing that 0.9558 Gm. of tin had been changed by the nitric acid present, this in turn being multiplied by the factor 0.1144, (obtained by dividing the eq. of nitric acid by eight times the eq. of tin,) gave 0.10934 Gm.  $\text{NO}_2$ , theory requires that 0.2 Gm.  $\text{KO}, \text{NO}_2$  should contain 0.10693 Gm. In this case, therefore, the percentage of nitric acid in the salt was found to be 54.67, whereas it should be 53.41; but the mean of fifteen experiments made with variable quantities both of tin solution and nitrate, (always taking care that at least 10 eq. of tin were present for every one eq. of nitric acid,) gave 54.1 % instead of 53.41.

The titration with iodine may be entirely dispensed with by



distilling the ammonia from the tin solution after digestion, in the apparatus shewn in Fig. 11, in this case the liquid is simply neutralized with caustic soda or potash brought into the distilling flask, an excess of caustic alkali added, the contents of the flask boiled, as in § 16, the ammonia received into normal acid, and titrated in the ordinary way.

In case the substance under examination contains other matters affecting the tin solution, this plan may be adopted with advantage, but it is not so accurate as the process just described.

If sulphuric acid or a soluble sulphate is present in the substance digested with the solution of tin, sulphurous acid will be formed; sulphate of baryta is, however, not affected, consequently it is necessary to precipitate the sulphuric acid in the form of sulphate of baryta, previous to digestion, when the method of estimation by iodine is used.

**8. Estimation by the loss which occurs when a Nitrate is fused with Bichromate of Potash, Silicic Acid, or Borax.**

Though not a volumetric method, this is given here because of its simplicity of application and accuracy of results.

Many years ago, Schaffgotsch announced the use of fused borax for this purpose, and since then Persoz has recommended bichromate of potash, and Reich silica, both of which are preferable to borax, and have afforded Fresenius, Finkener, and many others, myself among the number, very accurate results; in neither case do sulphates or chlorides interfere.

With bichromate of potash the following plan is the best.

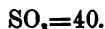
The well dried and weighed nitrate is mixed with two or three times its weight of freshly fused and powdered bichromate in a large platinum crucible, the cover laid on, the whole weighed, and a gentle heat applied, then gradually raised until the bottom of the crucible is of a dull red, and continued for three quarters of an hour; then a gas jet directed upon the

cover of the crucible, until bright red for a few minutes, in order that any particles of the mass which may have been projected against it may be thoroughly decomposed. The cover is then removed for a few minutes, then replaced, and the whole suffered to cool; when quite cold the weight is again taken and the loss reckoned as nitric acid. The results obtained in several experiments with pure nitre alone, or mixed with chlorides and sulphates, were 53·35, 53·39, 53·49, 53·44, &c., instead of 53·41.

With silica, four or five times the weight of nitrate is used, and the heat need not be so carefully regulated as with bichromate of potash. Twenty minutes or half an hour's red heat is sufficient; results with the same materials as above, 53·41, 53·54, 53·50, 53·6, 53·66, &c., instead of 53·41. In either case volatile substances, organic matter, &c., must of course be excluded.

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**SULPHURIC ACID.**



**Hydrated Sulphuric Acid.**



§ 27. 10 CC of concentrated white acid was weighed, and found to be 18·25 Gm., spec. grav. therefore 1·825.

In consequence of the great concentration and high spec. grav. of this acid, it is best to use only 1 or 2 CC for analysis; after the spec. grav. is taken, 1 CC may be titrated, taking care that a very fine and accurate pipette is used for the purpose, or if this is not at hand, it must be weighed direct upon the balance.

2 Gm. of the above acid was titrated, and found to require 37 CC of normal alkali, =90·65 % hydrated acid, which agrees exactly with Bineau's table.

**SULPHURIC ACID IN COMBINATION.**

§ 28. 1. The indirect process devised by C. Mohr, and fully described in the "Annalen der Chemie und Pharmacie," Bd. 90, S. 165, depends upon the same method of determination as has already been described for the alkaline earths, that is to say, a known volume of baryta solution is added to the compound, more than sufficient to precipitate the sulphuric acid, the excess of baryta is converted into carbonate, and titrated with normal acid and alkali, as described in § 17.

It is best to use a normal solution of chloride of barium as the precipitant, which is made by dissolving 122.05 Gm. of purest chloride in the litre; this solution likewise suffices for the determination of sulphuric acid by the direct method.

The following is the best method of procedure.

If the substance contains a considerable quantity of free acid, it must be brought near to neutrality by carbonate of soda, (perfectly free from  $\text{SO}_3$ ) if alkaline, to be slightly acidified with hydrochloric acid, a round number of CC of baryta solution is then added, and the whole digested in a warm place for some minutes; then precipitate the excess of baryta by a mixture of carbonate and caustic ammonia in slight excess, if a little piece of litmus paper be thrown into the mixture, a great excess can readily be avoided. The precipitate containing both sulphate and carbonate is now to be collected on a filter, and thoroughly washed with boiling water, then titrated as in § 17.

The difference between the number of CC of baryta solution added, and those of normal acid required for the carbonate, will be the measure of the sulphuric acid present, each CC of baryta solution is equal to .040 Gm.  $\text{SO}_3$ .

Example: 2 Gm. pure and dry nitrate of baryta, and 1 Gm. pure sulphate of potash were dissolved, mixed, and precipitated hot with carbonate and caustic ammonia, the precipitate, after being thoroughly washed, gave 1.002 Gm. sulphate of potash, instead of 1 Gm.

2 Gm. pure anhydrous sulphate of soda was dissolved, and 35 CC of normal chloride of barium added; 6.8 CC normal nitric acid were necessary to decompose the residual carbonate of baryta, therefore 28.2 CC of baryta solution was required to combine with the sulphuric acid present, this multiplied by .071 gave 2.002 Gm.  $\text{Na O SO}_3$  instead of 2 Gm. With Mohr the results were equally satisfactory.

**2. Titration by Chloride of Barium, with Chromate of Potash as indicator, (Wildenstein.)**

In Fresenius' "Zeitschrift für Analytische Chemie," part 3, Wildenstein has announced a new method for the more rapid and secure estimation of sulphuric acid, the principle of which is as follows:—

To the hot and somewhat concentrated sulphuric acid solution, (which must be neutral, or if acid, neutralized with caustic ammonia, free from carbonate,) a standard solution of chloride of barium is added in slight excess, then a solution of neutral chromate of potash, of known strength, is cautiously added to precipitate the excess of baryta; so long as any baryta remains in excess, the supernatant liquid is colourless, when it is all precipitated the liquid is yellow, from the free chromate of potash; as a few drops only of a solution of chromate are necessary to produce a distinct colour, the process is capable of very good results.

The standard solution of chloride of barium may be normal, that is, 122.05 Gm. per litre, 1 CC = 0.040 Gm.  $\text{SO}_3$ . The chromate of potash also normal = 97.35 Gm., per litre, 1 CC = 0.040 Gm.  $\text{SO}_3$ , or 0.122 Gm. Ba Cl.

The use of solutions of this strength, however, necessitates great care in the analytical process, lest the end of reaction should be overstepped too hastily, but it has the convenience of requiring little calculation.

Wildenstein uses a chloride of barium solution, of which 1 CC= $0.015$  Gm.  $\text{SO}_3$ , and chromate of potash 1 CC= $0.010$  Gm.  $\text{SO}_3$ . It would, I think, be preferable to use seminormal solutions, so that 1 CC of each would be equal to  $0.020$  Gm.  $\text{SO}_3$ . If the chromate solution is made to possess the same chemical power as that of the chloride, the operator has simply to deduct the one from the other in analysis, in order to obtain the quantity of chloride of barium really required to precipitate all the sulphuric acid.

The analytical process.—The substance or solution containing sulphuric acid is brought into a small wide-mouthed flask, diluted to about 50 CC, if acid, neutralized with pure ammonia in slight excess, heated to boiling, and the chloride of barium solution delivered cautiously from the burette, till in slight excess; as the precipitate rapidly settles from a boiling solution, it is not difficult to avoid great excess of baryta, which would prevent the liquid from clearing so speedily.

The flask is then put over the lamp again, heated to boiling, and the chromate solution added in  $\frac{1}{2}$  CC or so, each time removing the flask from the lamp, and allowing to settle until the supernatant liquid is of a light yellow colour; the quantity of chromate solution is then deducted from the baryta, and the remainder calculated for  $\text{SO}_3$ .

Or the mixture with baryta in excess may be diluted to 100 or 150 CC, the precipitate allowed to settle thoroughly, and 25

50 CC of the clear liquid taken out, heated to boiling, and precipitated with chromate until all the baryta is carried down as chromate of baryta, leaving the supernatant liquid of light yellow colour; if there is any uncertainty in the first titration, the analysis may be checked by a second. Wildenstein obtained very good results by this process, as the following statements will shew.

A mean of seven estimations of the sulphuric acid in sulphate of magnesia gave  $32.75\%$  instead of  $32.34$  required by theory; a mean of six for  $\text{SO}_3$  in sulphate of soda,  $55.85\%$ .

instead of 56.34; a mean of ten for  $\text{SO}_4$  in sulphate of potash, 45.06 instead of 45.92; in sulphate of alumina and potash 33.58 instead of 33.73; in sulphate of iron and ammonia, 41.4 instead of 40.82. For technical purposes the process is therefore very satisfactory.

### 3. Direct Precipitation with Normal Chloride of Barium.

Very good results may be obtained by this method when carefully performed. The substance in solution is to be acidified with hydrochloric acid, heated to boiling, and the baryta solution allowed to flow cautiously in from the burette until no further precipitation occurs. The end of the process

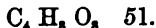


Fig. 15.

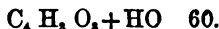
can only be determined by filtering a portion of the liquid, and testing with a drop of the baryta solution. Dr. Beale's filtering tube, shewn in Fig. 15, is the best aid in this case; a piece of fine filtering paper is tied over the lower end, which is then to be dipped about half an inch into the liquid, which rises into the tube perfectly clear; a little is to be poured into a test tube and a drop of baryta added from the burette; if a cloudiness occurs, the contents of the tubes must be emptied back again, washed out into the liquid, and more baryta added until all the sulphuric acid is precipitated; a decinormal solution of baryta is advisable towards the end of the process.

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### ACETIC ACID.



#### Monohydrated Acetic Acid.



§ 29. In consequence of the anomaly existing between the specific gravity of acetic acid and its strength, the hydrometer

gives no uniformly reliable indication of the latter, and consequently the volumetric method is peculiarly suitable for ascertaining the value of acetic acid in all its forms. For most technical purposes, normal caustic alkali may be used as the saturating agent; but a slight error occurs in this method from the fact that neutral acetates have an alkaline reaction on litmus; the error, however, is very small, if care be taken to add the alkali till a distinct blue colour is reached. As acetic acid is volatile at high temperatures, normal carbonate of soda must not be used for titrating it, as it would necessitate heat to expel the carbonic acid.

Example: 5 CC of Beaufoy's acetic acid weighed 5.206 Gm. = 1.041 spec. grav. The quantity of normal alkali required to saturate it was 27.1 CC, which multiplied by 0.51 = 1.382 Gm. anhydrous acetic acid, or 26.54 %. As the spec. grav. of commercial acetic acid varies very slightly, being generally 1.04, it is sufficient for many purposes to dispense with the trouble of weighing, and to use the pipette only; in order that 1 CC of normal alkali should represent one per cent. of acid, one tenth of the atomic weight, = 5.1 Gm., must be taken, consequently  $\frac{5.1}{1.04} = 4.904$  CC, so that, generally speaking, 4.9 CC taken with the pipette, will be the same as 5.1 Gm. by the balance. 4.9 CC of the same acid as above was titrated, and required 26.5 CC = 26.5 %. For the ordinary vinegars, there is no necessity to take the spec. grav. into the question. 5 or 10 CC may be taken as 5 or 10 Gm. Malt or coloured vinegar must be copiously diluted, in order that the change in the colour of the litmus may be distinguished; where the colour is such as to make the end of the process doubtful, recourse must be had to litmus paper, upon which little streaks should be made from time to time with a fine glass rod or a small feather.

Several processes have at various times been suggested for the *accurate and ready* estimation of acetic acid, among which I may mention that of C. Greville Williams, by means of a

standard solution of lime syrup, the results he obtained seemed very satisfactory, but where absolute accuracy is required in every possible form and colour of acetic acid, C. Mohr's process is undoubtedly the most reliable.

It consists in adding to a known quantity of the acid an excess of carbonate of baryta or lime in fine powder, the pure carbonate of lime described in the chapter on alkaline earths is preferable, as it dissolves more readily than the baryta. When the decomposition is as nearly as possible complete in the cold, the mixture must be heated to expel the carbonic acid, and to complete the saturation; the residual carbonate is then brought upon a filter, washed with boiling water, and titrated with normal acid and alkali.

This process is applicable in all cases, and however dark the colour may be, in testing the impure brown pyroligneous acid it is especially serviceable. For all ordinary kinds of acetic acid and vinegar, however, the quickest and most accurate test is Kieffer's ammonio-sulphate of copper solution for acidimetry, the preparation and use of which will now be described.

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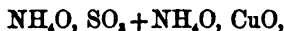
NORMAL AMMONIO-SULPHATE OF COPPER.

§ 30. This acidimetric solution is prepared by dissolving pure sulphate of copper in warm water, and adding to the clear solution liquid ammonia, until the bluish green precipitate which first appears is nearly dissolved; then filtered into the graduated cylinder, and titrated by allowing it to flow from a pipette graduated in  $\frac{1}{2}$  or  $\frac{1}{10}$  CC, into 10 or 20 CC of normal sulphuric or nitric acid, (not oxalic;) while the acid remains in excess, the bluish green precipitate which occurs as the drop falls into the acid rapidly disappears, but so soon as the exact point of

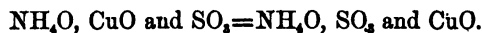


saturation occurs, the previously clear solution is rendered turbid by the precipitate remaining insoluble in the neutral liquid; the principle is as follows.

The copper solution has the composition—



it is in the latter half of the formula that the acidimetric power is contained, for when the solution is brought into contact with free sulphuric or other admissible acid, the latter combines with the ammonia; while there is a trace of free acid present, the oxide of copper is dissolved as soon as precipitated, but immediately the saturation is complete it remains precipitated; so that the decomposition is in the case of sulphuric acid—



The process is especially serviceable for the estimation of the free acid existing in certain metallic solutions, i.e., mother liquors, &c., where the neutral compounds of such metals have an acid reaction on litmus,—such as the oxides of zinc, copper, and magnesia, and the protoxides of iron, manganese, cobalt, and nickel,—it is also applicable to acetic and the mineral acids.

The value of the process in any given case depends upon the insolubility of the cupric oxide in the neutral solution which results from the combination of the ammonia and acid. M. Carey Lea (*vide* "Chemical News," Oct. 12th, 1861, p. 196) has objected to this process on the ground that the precipitate (which he supposes to be a basic sulphate of copper) is not totally insoluble in certain neutral solutions when concentrated, such as sulphate, nitrate, and chloride of ammonium, and he thinks it strange that so experienced a chemist as Mohr should be led into the error of highly recommending such an acidimetric process, alleging that a different result would be obtained between testing a solution containing 5 Gm. of sulphuric acid with 5 Gm. of sulphate of ammonia and the same quantity of

acid, with 20 or 50 Gm. of sulphate of ammonia; very probably this would be the case, but as it is an assumption which would not be likely to occur in practice, it does not invalidate the accuracy of the process when proper precautions are taken. Mohr especially mentions that the solutions to be tested should be dilute, and it is not likely that any experienced analyst would operate upon the large quantities alluded to by the objector.

In the first edition of Mohr's "Titrimethode," the author records an experiment on the determination of oxide of magnesia by this method, wherein a loss of four per cent. occurred; this M. Lea supposes to arise from the faultiness of the process, but as in the second edition Mohr recommends it for the determination of the same substance, and omits any mention of the former result, I suppose the error must have been owing to other causes. The process has given me good results, as may be seen under the head of magnesia. Fresenius also notices the process favourably in the last edition of his "Quantitative Analysis." More recently the same authority ("Zeitschrift für Analytische Chemie," 1, p. 108) has published a series of experiments, for the purpose of testing the truth of Lea's objection. The result is that he still recommends the process for technical purposes.

It is necessary from time to time to titrate the solution afresh, as it alters very slightly by keeping. I have found it to weaken to the extent of  $\frac{1}{2}$  per cent. in two years, when set aside in a bottle untouched. Where it is continually in use, and being freshly prepared every few weeks or days, the variation would be quite insignificant.

If nitrate of copper be used instead of sulphate in the preparation of the normal solution, the presence of baryta, strontian, lead, and silver, in the acid solution is of no consequence.

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**TESTING OF ACETIC ACID OR VINEGAR BY AMMONIO-SULPHATE  
OF COPPER.**

§ 31. THE only necessary condition is that the acid be very dilute, as the copper precipitate is soluble in concentrated acetate of copper; if the first drop of copper solution produces a turbidity which disappears only on shaking or stirring the liquid, the dilution is sufficient; and in order that the first traces of a permanent precipitate may be recognised, it is well to place a piece of dark coloured paper under the beaker. The results are very uniform and reliable.

For the vinegars of commerce, this process seems peculiarly applicable, as a large amount of dilution is of no consequence to the reagent, and owing to the colour of malt vinegar it is of considerable value to the analyst, as it enables him to distinguish the end of the process more exactly.

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**ESTIMATION OF CERTAIN METALLIC OXIDES OR THEIR NEUTRAL  
SALTS IN ACID SOLUTIONS, TOGETHER WITH THE FREE  
ACID BY KIEFFER'S SOLUTION.**

§ 32. THAT the objection made by Lea to this acidimetric method had a nucleus of truth in it, no one would doubt who knows something of that accomplished chemist, but when tolerably dilute cold solutions are used, and some little practice obtained, the results are uniformly good, and susceptible of a great amount of accuracy. As the process is mostly available for technical uses, it is amply sufficient for the purpose. The oxides and carbonates of zinc and magnesia are first dissolved in a known quantity of normal nitric or sulphuric acid, and then titrated backward with normal copper solution.

Example, 3.9 Gm. of Howard's calcined magnesia was dissolved in 220 CC of normal sulphuric acid, and 3.0 CC of

copper solution added, whose factor for normal strength was  $\cdot 909 = 27\cdot 27$  CC normal, which deducted from 220 leaves  $192\cdot 7$  CC of normal acid  $= 3\cdot 86$  Gm. pure magnesia, or 99 per cent ; there was a small amount of insoluble matter which would probably make up the difference. For this large quantity of material the result is very satisfactory.

1 Gm. of pure and freshly ignited oxide of zinc was dissolved in 27 CC of normal nitric acid, and  $2\cdot 3$  CC of copper solution required  $= 24\cdot 7$  CC acid, which multiplied by  $\cdot 04053$ , gave  $1\cdot 001$  Gm.

20 Gm. of an acid solution of sulphate of zinc was taken from the cell of a Smee's battery, and titrated with the copper solution, of which  $18\cdot 5$  CC were required to produce a precipitate ; this multiplied by  $\cdot 040$  Gm., gave  $\cdot 74$  Gm.  $= 3\cdot 7$  % of sulphuric acid in a free state.

Acid mother liquors of green and blue copperas can be examined in the same way.

## ORGANIC ACIDS.

## § 33.

Substance.	Formula.	Atomic Weight	Quantity to be weighed so that 1 CC. or 1 dm. N. alk. = 1 per cent. of substance.	Normal Factor.
Tartaric Acid (cryst.)	$C_4 H_4 O_6 + HO$	75	75 Gm., or 750 grn.	$0\cdot 075$ , or $0\cdot 75$
Bitartrate of Potash (argol)	$KO, 2C_4 H_4 O_6 + HO$	188·11	$18\cdot 811$ Gm., or $188\cdot 11$ grn.	$0\cdot 18811$ , or $1\cdot 8811$
Citric Acid (cryst.) ...	$C_6 H_8 O_7 + HO$	69	69 Gm., or 690 grn.	$0\cdot 069$ , or $0\cdot 69$
Oxalic Acid (cryst.)...	$C_2 O_3 + 3HO$	63	63 Gm., or 630 grn.	$0\cdot 063$ , or $0\cdot 63$
Binoxalate of Potash (sal. acetosella)	$KO, 2C_2 O_3 + 3HO$	146·11	$14\cdot 611$ Gm., or $146\cdot 11$ grn.	$0\cdot 14611$ , or $1\cdot 4611$

Normal caustic alkali is the best agent for titrating the substances contained in the above table.

**ESTIMATION OF COMBINED ACIDS IN NEUTRAL SALTS.**

§ 34. THIS comprehensive method of determining the quantity of acid in neutral compounds, (but not the nature of the acid), is applicable only in those cases where the base is perfectly precipitated by an excess of caustic alkali or its carbonate. The number of bodies capable of being so precipitated is very large, as has been proved by the researches of M. M. Langer and Wawnikiewicz, (*Ann. der Chemie und Pharm.*, p. 239, Feb. 1861,) who seem to have worked out the method very carefully. These gentlemen attribute its origin to Bunsen; but it does not seem certain who devised it. The best method of procedure is as follows:—

The substance is weighed, dissolved in water in a 300 CC flask, heated to boiling or not, as may be desirable, then adding, from a burette, normal alkali or its carbonate, according to the nature of the base, until the whole is decidedly alkaline. dilute to 300 CC and put aside to settle; 100 CC are then taken out and titrated for the excess of alkali; the remainder multiplied by 3, gives the measure of the acid combined with the original salt, i.e., supposing the precipitation is complete.

Example. 2 Gm. crystals of chloride of barium were dissolved in water, heated to boiling, and 20 CC normal carbonate of soda added, diluted to 300 CC, and 100 CC of the clear liquid titrated with normal nitric acid, of which 1.2 CC were required—altogether, therefore, the 2 Gm. required 16.4 CC normal alkali—this multiplied by 0.122, gave 2.0008 Gm. Ba Cl, instead of 2 Gm.; multiplied by the factor for chlorine 0.03546, it yielded 0.58154 Gm., theory requires 0.5813 Gm. chlorine.

The following substances have been submitted to this mode of examination with satisfactory results:—

Salts of the alkaline earths precipitated, boiling hot, with an alkaline carbonate.

Salts of magnesia, with pure or carbonated alkali.

Alum, with carbonate of alkali.

Zinc salts, boiling hot, with the same.

Copper salts, boiling hot, with pure potash.

Silver salts, with pure alkali.

Bismuth salts, half-an-hour's boiling, with carbonate of soda.

Nickel and Cobalt salts, with carbonate of soda.

Lead salts, with the same.

Iron salts, boiling hot, with pure or carbonated alkali.

Mercury salts, with pure alkali.

Protosalts of manganese, boiling hot, with carbonate of soda.

Chromium persalts, boiling hot, with pure potash.

Where the compound under examination contains but one base precipitable by alkali, the determination of the acid gives, of course, the quantity of base also.

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## APPENDIX TO PART II.

## TECHNICAL EXAMINATION OF COMMERCIAL ALKALINE PRODUCTS.

## Soda Ash or Alkali.

§ 35. **MOISTURE** must be determined by heating 5 or 10 Gm. to dull redness for ten minutes, in a small crucible of platinum, silver, iron, or porcelain, allowing it to cool under a bell glass in the presence of sulphuric acid or chloride of calcium: the difference between the first and second weighings is the accidental moisture in the sample.

The contents of the crucible are then dissolved in about four ounces of warm distilled water, and any insoluble matter filtered off by a small filter, the latter washed a few times with hot water, then, if necessary, dried, ignited, and weighed as insoluble matter. It is important that this insoluble matter be removed before titration, otherwise the lime and other constituents in it will consume a portion of the normal acid, and so register a higher percentage of alkali than is really present.

The total quantity of alkali is determined in a measured portion of the filtrate and washings previously diluted up to  $\frac{1}{2}$  or 1 litre, by normal sulphuric or oxalic acid, as in § 12.

The quantity of caustic alkali present in any sample is determined as in § 15.

The presence of sulphide of sodium is ascertained by the smell of sulphuretted hydrogen when the alkali is saturated

with an acid, or by dipping paper, steeped in nitro-prusside of sodium, into the solution, if the paper turns blue or violet sulphide is there.

The quantity of sulphide and hyposulphite of sodium may be determined by saturating a dilute solution of the alkali with a slight excess of acetic acid, adding starch liquor, and titrating with decinormal iodine solution (§ 45) till the blue colour appears. The quantity of iodine required is the measure of the sulphuretted hydrogen and hyposulphurous acid present. The quantity of each may be known by adding a solution of sulphate of zinc to a like quantity of the alkali, and filtering so as to remove the free carbonated and sulphuretted alkali, by which means the hyposulphurous acid alone remains, which may be estimated with iodine and starch as before, the quantity of iodine solution so required is to be deducted from the total, and the calculation for both sulphide and hyposulphite of sodium may then be made, 1 CC decinormal iodine is equal to .0248 Gm. hyposulphite of soda, or .0039 Gm. sulphide of sodium; good English alkali is seldom contaminated with these substances to any extent.

Chloride of sodium (common salt) may be determined by neutralizing .585 Gm. or 5.85 grn. of the alkali with nitric acid, and titrating with decinormal silver solution and chromate of potash, (§ 74). Each CC or dm. corresponds to 1 per cent. of common salt, if the above weight is taken.

Sulphate of soda is determined, either direct or indirect, as in § 28, each CC or dm. of normal chloride of barium is equal to .071 Gm., or .71 grn. of dry sulphate of soda.

Black ash and raw mother liquors and lyes can be examined in precisely the same way as above; if oxide of iron is present it may be determined as in § 47; lime, by boiling with carbonate of soda and precipitation as carbonate—washing the precipitate thoroughly with boiling water, and titration with normal acid and alkali, as in § 18. Phosphoric acid with uranium solution, as in § 78, 1.



**POTASH AND PEARLASH**

§ 36. ARE examined in the same way as soda.

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**SALT CAKE**

§ 37. Is the impure sulphate of soda left in the retorts in preparing hydrochloric acid from sulphuric acid and salt. It generally contains free sulphuric acid existing as bisulphate of soda, the quantity of which may be ascertained by direct titration with normal alkali.

The common salt present is estimated by decinormal silver solution and chromate of potash; having first saturated the free acid with pure carbonate of soda, see § 74, 1 CC or 1 dm. silver solution, is equal to .005846 Gm. or .05846 grn. of salt.

Sulphuric acid, combined with soda, is estimated either directly or indirectly as in § 28; 1 CC or 1 dm. of normal baryta solution is equal to .071 Gm., or .71 grn. of dry sulphate of soda.

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**RAW SALT, BRINE, &c.**

§ 38. LIME may be estimated by precipitation with oxalate of ammonia, and the precipitate titrated with permanganate, as in § 60, 1.

Sulphuric acid as in § 28.

Magnesia is precipitated as ammoniacal phosphate, by a solution of phosphate of soda containing ammonia, first removing the lime by oxalate of ammonia, the precipitate of double phosphate of magnesia and ammonia is brought on a filter, washed with cold water containing ammonia, then dis-

solved in acetic acid, and titrated with uranium solution, as in § 78, 1; each CC of solution required represents 0.0563 Gm. magnesia; or the precipitate may be dried, ignited, and weighed as pyrophosphate of magnesia.

The quantity of real salt in the sample may be ascertained by treating a weighed quantity in solution with caustic baryta, boiling, setting aside that the excess of baryta may precipitate itself as carbonate, or more quickly by adding carbonate of ammonia, filtering, evaporating the solution to dryness, and gently igniting—the residue is pure salt. The loss of weight between this and the original specimen taken for analysis, will shew the percentage of impurities.

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**GYPSUM, SELENITE, PLASTER OF PARIS,**

§ 39. MAY be estimated direct by boiling a weighed quantity, in fine powder, with its own weight of carbonate of soda and about 20 parts water, for half-an-hour, adding fresh water to supply the waste; the carbonate of lime so formed is brought upon a filter, washed thoroughly with boiling water, and the precipitate and filter titrated with normal acid and alkali, as in § 18.

Sulphuric acid may be estimated in the filtrate from above, directly or indirectly, by normal chloride of barium, as in § 28.

The indirect estimation of gypsum is obtained by boiling 3 Gm. with 60 CC of normal carbonate of soda for some time in a 300 CC flask, dilute to the 300 CC mark, and put aside to settle, take out 100 CC of the clear liquid with a pipette, and titrate with normal acid and alkali, multiply the quantity of acid by 3, and deduct the product from the original 60 CC of alkali. The remainder is calculated as hydrated sulphate of lime, by multiplying with .086, or as anhydrous with .068. Principle of the process explained in § 34.

**AMMONIACAL GAS LIQUOR.**

§ 40. THE value of this substance depends upon the quantity of ammonia contained therein, this constituent mainly exists in a free state, some portion of it, however, generally exists as sulphide and hyposulphite of ammonium. The free alkali is best determined by titrating a known volume of the liquor with normal acid and litmus; in consequence of the dark colour and other contaminations of the liquor, it is more secure to ascertain the end of the process by litmus paper—a glass rod or small feather moistened with the mixture may be brought in contact with both red and blue paper, when both remain unaffected the process is finished; each CC or dm. of acid is equal to  $\cdot 017$  Gm., or  $\cdot 17$  grn. of ammonia.

The total quantity of ammonia is ascertained by distilling a portion of the gas liquor in the apparatus, Fig. 11. Or an equally exact process, when the liquor contains no other salt than ammonia, consists in saturating a portion of the liquor with pure hydrochloric acid, and evaporating to perfect dryness on the water-bath; then heating the residue to about  $240^{\circ}$  Fahr. in the sand or air-bath, dissolving in water, filtering and titrating with decinormal silver solution and chromate of potash, as in § 75.

Each CC or dm. of  $\frac{N}{10}$  silver solution, is equal to  $\cdot 0017$  Gm. or  $\cdot 017$  grn. of ammonia.

Hydrosulphuric and hyposulphuric acids can be estimated with  $\frac{N}{10}$  iodine solution, as in the case of alkali. (§ 35.)

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**ALKALINE NITRATES, (SALTPETRE, NITRATE OF SODA, &c.)**

§ 41. IN the case of saltpetre and nitrate of soda, the nitric acid is determined in the previously fused samples by ignition

with bichromate of potash or silicic acid, as in § 26, 8; or by any more convenient method in the same section.

Chlorine, existing as common salt, is determined as in § 74; sulphuric acid, direct or indirect, as in § 28; lime is precipitated as carbonate, and titrated as in § 18.

When mixtures of nitrate of potash and soda occur, the potash must be determined by precipitation as double chloride of platinum and potassium.

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## PART III.

## ANALYSIS BY OXIDATION AND REDUCTION.

## INTRODUCTION.

§ 42. THE series of analyses which occur under this system are very extensive in number, and not a few of them possess extreme accuracy, such in fact as is not possible in any analysis by weight, consequently they have now been established, whenever practicable, instead of the old system. The completion of the various processes is generally shown by a distinct change of colour, such for instance as the occurrence of the beautiful rose red permanganate or the blue iodide of starch, and as the smallest quantity of these substances will colour distinctly large masses of liquid, the slightest excess of the oxidising material is sufficient to produce a satisfactory result.

The principle involved in the processes is extremely simple. Substances which will take up oxygen are brought into solution, and titrated with a substance of known oxidising power—such for instance as occurs in the determination of protoxide of iron by permanganate of potash. The iron is ready and willing to receive the oxygen, the permanganate is equally willing to part with it; while the iron is absorbing the oxygen the permanganate loses its colour almost as soon as it is added, and the whole mixture is colourless, but immediately the

iron is satisfied the rose colour no longer disappears, there being no more oxidisable iron present. 2 atoms FeO absorb 1 atom oxygen, becoming 1 atom  $\text{Fe}_2\text{O}_3$ . Oxalic acid occupies the same position as protoxide of iron, its composition is  $\text{C}_2\text{O}_3 + 3\text{Aq.}$ ; if permanganate is added to it 1 atom combines with 1 atom oxygen and is resolved into 2 atoms carbonic acid; when the oxalic acid is all decomposed the colour of the permanganate no longer disappears. On the other hand, substances which will give up oxygen are deoxidised by a known excessive quantity of reducing agent, the amount of which excess is afterward ascertained by residual titration with a standard oxidising solution; the strength of the reducing solution being known, the quantity required is a measure of the substance which has been reduced by it.

The oxidising agents best available are—permanganate of potash, iodine, bichromate of potash, and red prussiate of potash.

The reducing agents are—sulphurous acid, hyposulphite of soda, oxalic acid, protoxide of iron, arsenious acid, protochloride of tin, yellow prussiate of potash and zinc.

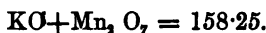
With this variety of materials a great many combinations may be arranged so as to make this system of analysis very comprehensive, but the following are given as sufficient for almost all purposes, and as being susceptible of the greatest amount of purity and stability of material, with exceedingly accurate results :—

1. Permanganate and protoxide of iron, (with the rose colour as indicator); permanganate and oxalic acid, (with the rose colour as indicator).
2. Bichromate of potash and protoxide of iron, (with cessation of blue colour, when brought in contact with red prussiate of potash, as indicator).
3. Iodine and hyposulphite of soda, (with starch as indicator); iodine and arsenite of soda, (with starch as indicator).

## PREPARATION OF STANDARD SOLUTIONS.

## PERMANGANIC ACID AND PROTOXIDE OF IRON.

## Permanganate of Potash.



§ 43. THE solution of this salt is best prepared for analysis by dissolving the pure crystals in distilled water of such a strength that 17.85 CC will peroxidise 1 decigramme of iron. The solution is then decinormal. If well kept, it holds its strength several months.

The pure permanganate may be obtained very generally of the dealers in pure chemicals, but should it not be procurable, when required, or the expense too great, the solution may be prepared as follows:—

Ten parts of caustic potash and 7 of chlorate of potash are fused in a hessian crucible, then 8 parts of finely powdered peroxide of manganese added, and the whole well mixed with an iron rod; the crucible is kept at a dull red heat, and the contents stirred until, from the dissipation of the water, the mass loses its pasty state and becomes somewhat friable, continue the dull red heat, breaking the mass from the sides of the crucible and mixing altogether for a few minutes, then empty the contents into a clean copper or iron dish. When cool, it is to be coarsely powdered, put into a large flask or porcelain dish, and 20 or 30 times its weight of boiling water poured over it, then kept boiling gently until the solution assumes a deep purple rose colour. When the precipitated oxide of manganese has somewhat settled, the solution may be decanted into a large green glass bottle, and further diluted with the washings of the residue in the dish or flask to about the strength required for analysis. The solution so prepared con-

tains a large quantity of alkali, and is constantly undergoing a slight change owing to its containing a portion of manganate of potash which slowly decomposes with precipitation of oxide of manganese. If the excess of caustic potash is saturated by an acid, the solution is far more stable. Mulder, therefore, recommends that a stream of carbonic acid should be passed through the solution, frequently shaking it, until the potash is saturated; an excess of acid does no harm; sulphuric acid may also be used for the same purpose, but is not so recommendable.

When the liquid thus treated has thoroughly settled, a portion may be decanted (not filtered through paper) into a convenient sized bottle for laboratory use.

A very useful form of bottle for preserving it is the ordinary wash bottle, or any common bottle fitted with the same arrangement of tubes. Burettes can then be filled with the solution without its frothing, and as the tube which enters the liquid does not reach the bottom of the bottle, the sediment, if any, is not disturbed; another advantage is, that the solution does not come into contact with the cork, nor can any dust enter: the blowing tube may be closed by a very small cork.

A solution prepared and kept as here directed will generally preserve its strength unaltered for six months.

#### 1. Titration of the Permanganate Solution.

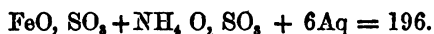
In order to ascertain the strength of the permanganate it must be titrated with either a weighed quantity of metallic iron, oxalic acid, or the double sulphate of iron and ammonia.

This latter salt is a most convenient substance for titrating the permanganate, as it saves the time and trouble of dissolving the iron, and being perfectly stable when pure, it can be depended on without risk. To prepare it, 139 parts of the purest crystals of protosulphate of iron, and 66 parts of pure crystallized sulphate of ammonia are separately dissolved in the least possible quantity of distilled water of about 120 Fahr. temp., if



the solutions are not perfectly clear they must be filtered; mix them at the same temperature in a porcelain dish, adding a few drops of pure sulphuric acid, and stir till cold, during the stirring the double salt will fall in a finely granulated form, set aside for a few hours, then pour off the supernatant liquor, and empty the salt into a clean funnel with a little cotton wool stuffed into the neck; so that the mother liquor may drain away, the salt may then be quickly and repeatedly pressed between fresh sheets of clean filtering paper, or still better, as Mohr recommends, dried in a centrifugal machine. As very few persons are possessed of this latter, albeit a most useful article, the salt may be spread out on a tray made of filtering paper, and the superfluous moisture driven off by a fan or pair of bellows; lastly, place it in a slightly warm place to dry thoroughly so that the small grains adhere no longer to each other or to the paper in which they are contained, then preserve it in a stoppered bottle for use.

The formula of the salt is—



Consequently it contains exactly one-seventh of its weight of iron, therefore, 0.7 Gm. represent 0.1 Gm. of iron, and this is a convenient quantity to weigh for the purpose of titrating the permanganate.

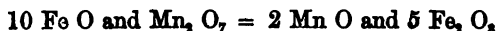
0.7 Gm. being brought into dilute solution in a flask or beaker, and 5 or 6 CC of dilute sulphuric acid (1 to 5) added, (the titration of permanganate, or any other substance, by it must always take place in the presence of free acid and preferably sulphuric), the permanganate is delivered from a Gay Lussac's plain, or with blowing tube, or the elastic ball burette divided in  $\frac{1}{2}$  or  $\frac{1}{10}$  CC, until a point occurs, when the rose colour no longer disappears on shaking; a few drops of the permanganate in excess are sufficient to produce this effect, but the actual quantity required to colour the same quantity of water should be found, and deducted from the total used

in the analysis. The titration is now ended, and the number of CC used may be marked upon the bottle as the quantity for 0.1 Gm. Fe, or the factor found, which is necessary to reduce it to decinormal strength, or diluted to that strength at once.

## 2. Titration with Metallic Iron.

The purest iron to be obtained is the thin annealed binding-wire free from rust. About 0.1 Gm. of this is to be dissolved in dilute sulphuric acid by the aid of heat, in a small flask closed with a cork, through which a fine glass tube is passed, so that the hydrogen which is evolved escapes under pressure, thus preventing the access of air; or better than this, the plan suggested by Mohr may be used, which consists in passing the upper end of the fine tube through a cork; over the end of the glass tube, which is level with the cork, a small piece of sheet india rubber or oiled silk is laid and pinned down to the cork with a pin on each side of the hole. This contrivance acts as a valve by which the hydrogen escapes from the flask under pressure, but so soon as the pressure of gas ceases and the flask cools, the valve closes by atmospheric pressure and thus prevents the entrance of air; by this means there is no difficulty in obtaining the whole of the iron in solution as protoxide. When the iron is all dissolved the flask may be two-thirds filled with cold distilled water, and the titration with permanganate commenced and concluded as in the case of the double sulphate.

The decomposition which ensues from treating protoxide of iron by permanganic acid may be represented as follows:—



therefore, 2 atoms of protoxide absorb 1 atom of oxygen and are changed into 1 atom of peroxide, consequently, in the systematic tables for iron given further on, (§ 47), the weight of the protoxide with its compounds is doubled.

### 3. Titration with Oxalic Acid.

About 0.63 Gm. of the pure acid is to be weighed, or 10 CC of normal solution measured with a pipette, brought into a flask with dilute sulphuric acid, as in the case of the iron salt, and considerably diluted with water, then warmed to about 80° Fahr. and the permanganate added from the burette. The colour disappears slowly at first but afterward more rapidly, becoming first brown, then yellow, and so on to colourless. More care must be exercised in this case than in the titration with iron, as the action is less decisive and rapid, nevertheless, it is as reliable with care and attention. 1 atom of oxalic acid takes up 1 atom of oxygen, and is resolved into 2 atoms of carbonic acid which escapes with faint effervescence; when the permanent rose colour appears the process is finished.

#### Precautions.

It must be borne in mind that free acid is always necessary in titrating a substance with permanganate, in order to keep the resulting oxide of manganese in solution. Sulphuric acid, in a dilute form, has no prejudicial effect on the pure permanganate, even at a high temperature; not so, however, nitric or hydrochloric acids, the former, though very dilute if it contain the lower oxides of nitrogen, immediately decomposes the solution, consequently the last traces of these must be removed by boiling previous to its addition. With hydrochloric acid the solution to be titrated must be very dilute and of low temperature, otherwise chlorine will be liberated and the analysis spoiled; under any circumstances the analysis must be subjected to correction with this acid, as will be shewn further on.

With the ordinary permanganate solution, prepared as previously described from chlorate and hydrate of potash and manganese, and which contains chloride of potassium, chlorine is liberated by sulphuric acid at a high temperature, therefore,

in any case it is advisable to use very dilute solutions at not more than 70° or 80° Fahr.

Organic matter of any kind decomposes the permanganate, and the solution, therefore, cannot be filtered through paper, nor can it be used in Mohr's burette, because it is decomposed by the india rubber tube.

It will be a startling announcement to the chemical world to be told that the determination of iron by permanganate, under many circumstances hitherto recommended, is subject to great error, so great an error in fact, that the determination may be totally worthless unless subjected to correction.

In Fresenius' "*Zeitschrift für Analytische Chemie*," part 3, (pub. in Oct. 1862.) Löwenthal and Lenssen have contributed a valuable paper on the subject, a short summary of which is as follows. A complete series of determinations of iron were made with different quantities of free hydrochloric and sulphuric acids, with variable quantities of water, free from air and containing air, and at various temperatures, correction being in all cases made for the quantity of solution of permanganate necessary to colour the various bulks of liquid.

The results proved conclusively that the process was exact only when the iron existed as sulphate, when a moderate quantity of free sulphuric acid was present, and when deduction was made for the colouration of the liquid. Fresenius has also most carefully checked the statements made by Löwenthal and Lenssen, obtaining results which point to the same conclusion. I give the experiments of Fresenius somewhat in detail. The permanganate solution was prepared with the pure crystals of such strength that 100 CC = 0.4 Gm. iron. The iron solution was prepared from pure sulphate. The hydrochloric and sulphuric acids used were absolutely pure, the first 1.12 spec. grav., the last 1.23; fresh distilled water was used for the dilution, and in order to remove any traces of reducing agents it was acidified with sulphuric acid, and sufficient permanganate added to give a permanent pinkish colour. The

correction, therefore, for colouration of the liquid was unnecessary.

Exp. 1, <i>a.</i> To 1 litre of the water so prepared,		
25 CC hydrochloric acid and 10		
CC iron solution were added.		
The permanganate required was.....		13.9 CC
<i>b.</i> To the same liquid 10 CC more of		
the iron solution was added, and		
required permanganate .....		12.9 "
<i>c.</i> Other 10 CC iron .....		12.9 "
<i>d.</i> Ditto .....		12.8 "
Exp. 2, <i>a.</i> 1 litre water, 25 CC sulphuric acid,		
and 10 CC iron required .....		13.1 "
<i>b.</i> Other 10 CC " .....		12.9 "
<i>c.</i> Ditto .....		12.9 "
Exp. 3, <i>a.</i> 1 litre water, 5 CC hydrochloric acid,		
and 10 CC iron .....		13.20 "
<i>b.</i> Other 10 CC iron .....		12.65 "
<i>c.</i> Ditto .....		12.62 "
Exp. 5, <i>a.</i> 1 litre water, 50 CC hydrochloric		
acid, and 10 CC iron, required...		14.30 "
<i>b.</i> Other 10 CC iron " .. ..		12.70 "
<i>c.</i> Ditto .....		12.68 "
Exp. 6, <i>a.</i> 1 litre water, 5 CC sulphuric acid,		
and 10 CC iron, required .....		12.98 "
<i>b.</i> Other 10 CC iron " .....		12.80 "
<i>c.</i> Ditto .....		12.80 "
Exp. 7, <i>a.</i> 1 litre water, 25 CC sulphuric acid,		
and 10 CC iron, required .....		12.88 "
<i>b.</i> Other 10 CC " .....		12.80 "
<i>c.</i> Ditto .....		12.80 "
Exp. 8, <i>a.</i> 1 litre water, 50 CC sulphuric acid,		
and 10 CC iron, required .....		13.20 "
<i>b.</i> Other 10 CC " .....		12.80 "
<i>c.</i> Ditto .....		12.80 "

No difference was discoverable when the quantity of water was lessened to one-fourth or increased to one litre, nor was any effect produced by adding perchloride of iron.

From the above experiments it will readily be seen that titration with permanganate is far less reliable in the presence of free hydrochloric than sulphuric acid, owing, undoubtedly, to some secondary reaction between the chlorine of the acid and the permanganate. All researches, however, go to prove that when a solution of the substance to be titrated with hydrochloric acid is divided into 3 or 4 portions, and successively titrated in the same liquid, the mean of the 2nd and 3rd, (setting the first entirely aside), will be dependable.

There can be very little doubt that the discrepancies shewn to occur in the use of hydrochloric acid will account, in some measure, for the frequent want of accuracy in Pelouze's method for the determination of nitrates and similar processes. It is, therefore, advisable, in all possible cases, to use sulphuric acid for acidifying the solution and to avoid any large excess.

Where hydrochloric acid must be used and bichromate of potash is not admissible for titration, the fractional estimation before-mentioned must be adopted, taking the second, or mean of second and third titrations as correct; where this is not practicable it is best to prepare a mixture of hydrochloric acid and water, add some sulphate of iron, and titrate with permanganate to the red tinge, then add the substance, and titrate with permanganate. Experiment has shown that this method is reliable.

#### **Examples of Iron Analysis with Permanganate.**

0.7 Gm. double iron salt = 0.1 Gm. iron, was carefully weighed, dissolved, and sulphuric acid added. Permanganate required was 10 CC; this was marked upon the label, and the bottle set aside in November, 1860. In July, 1862, the permanganate

solution was tested again and 0.7 Gm. double salt required 10.4 CC. This seems to prove that the solution is not so changeable as one is apt to suppose. I have, therefore, adopted the plan of keeping a decinormal solution, made by diluting the concentrated liquor obtained from the rough mass before described, and which holds its strength perfectly as yet, (October, 1862.)

0.5 Gm. pure sulphate of iron was titrated with the decinormal permanganate, of which 17.9 CC were required, this multiplied by 0.0278 gives 0.498 Gm. instead of 0.5 Gm.; as the crystals of sulphate of iron always contain a portion of mother liquor it is almost impossible to obtain a perfectly dry sample for examination, consequently there is an invariable loss in the analysis.

In using the decinormal permanganate it is advisable to operate upon small quantities of iron only, (1 or 2 decigrammes,) so that a small  $\frac{1}{10}$  CC burette may suffice.

#### Calculation of Analyses.

The calculation of analyses with permanganate, if the solution is not strictly decinormal, can be made by ascertaining its constant factor, reducing the number of CC used of it to decinormal strength, and multiplying the number of CC thus found by  $\frac{100}{1000}$  atom of the substance sought; for instance—

Suppose that 15 CC of permanganate solution have been found to equal 0.1 Gm. iron, it is required to reduce the 15 CC to decinormal strength, which would require 1000 CC of permanganate to every 5.6 Gm. iron, therefore  $5.6 : 1000 :: 0.1 : x = 17.85$  CC; 17.85 multiplied by 0.0056 = 0.09996 Gm. iron, which is as near to 0.1 Gm. as can be required. Or the factor necessary to reduce the number of CC used may be found as follows:— $0.1 : 15 :: 5.6 : x = 84$  CC, therefore,  $\frac{100}{84} = 1.19$ .

Consequently 1.19 is the factor by which to reduce the number of CC of that special permanganate used in any analysis to the

decinormal strength, from whence the weight of substance sought may be found in the usual way.

Another plan is to find the quantity of iron or oxalic acid represented by the permanganate used in any given analysis, and this being done the following simple equation gives the required result :—

$$\begin{array}{ccccccc} 2 \text{ at. Fe (56)} & \text{at. weight of} & \text{the weight} & \text{the weight of} & & & \\ \text{or} & : & \text{the substance} & :: & \text{of Fe or} & : & \text{substance} \\ 1 \text{ at. } \overline{\text{O}} \text{ (63)} & \text{sought} & \overline{\text{O}} \text{ found} & & \text{sought.} & & \end{array}$$

In other words, if the atomic weight of the substance analysed be divided by 56 or 63, (the respective atomic weights of iron or oxalic acid), a factor is obtained by which to multiply the weight of iron or oxalic acid, equal to the permanganate used, the product is the weight of the substance analysed.

For example, copper is the substance sought, 2 at. Cu corresponding to 2 at. Fe is 63·4, let this number, therefore, be divided by 56, whence  $\frac{63\cdot4}{56} = 1\cdot1314$ , therefore, if the quantity of iron represented by the permanganate used in a copper analysis, be multiplied by 1·1314, the product will be the weight of the copper sought.

Where possible the necessary factors will be given in the tables preceding any leading substance.

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#### CHROMIC ACID AND PROTOXIDE OF IRON.

Bichromate of Potash.

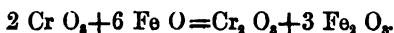


§ 44. THIS substance, which appears to have been first proposed by Professor Penny, of Glasgow, possesses the great advantage over permanganate, that it is absolutely per-



manent in solution, is very cheap, and may frequently be obtained in ordinary commerce in a pure state; beside which, its solution may be used in Mohr's burette without undergoing the change peculiar to permanganate; on the other hand, the end of the reaction in the estimation of iron can only be known by an external indicator, that is to say, a drop of the mixture is brought in contact with a drop of solution of red prussiate of potash (freshly prepared) upon a white slab or plate; while the protoxide of iron is in tolerable excess, a rich blue colour occurs at the point of contact between the drops, but as this excess continues to lessen by the addition of the bichromate, the blue becomes somewhat turbid, having first a green, then grey, and lastly brown shade. When the greenish blue tint has all disappeared, the process is finished. This series of changes in the colour admits of very sharp and sure reading of the burette, after a little practice is obtained.

The reaction between chromic acid and protoxide of iron may be represented by the formula,



The decomposition takes place immediately and at ordinary temperatures in the presence of free sulphuric or hydrochloric acid; nitric acid is, on account of the protoxide of iron, of course inadmissible.

The reduction of the compounds of iron to the state of protoxide may be accomplished by zinc or sulphurous acid as with permanganate; or instead of these, protochloride of tin may be used, which acts very rapidly as a reducing agent upon peroxide of iron, the red colour of the solution disappearing almost immediately.

In the analysis of iron ores this method of reduction is serviceable; the greatest care, however, is necessary, that the protochloride is not present in excess, as this would consume the bichromate solution equally with the protoxide of iron, and so lead to false results.

The discharge of the red colour of the iron solution may with care be made a very sure indication of the exact point of reduction. The concentrated hydrochloric solution of iron is heated to gentle boiling, and the moderately dilute tin solution added with a pipette, waiting a moment after each addition till the last traces of colour have disappeared; the solution is then poured into a beaker, diluted with water, and titrated with the bichromate as usual; an extra security is obtained by adding a few drops of sulphocyanide of potassium to the solution, the disappearance of the blood-red colour indicating that no more peroxide of iron is present.

In order to obviate the inaccuracy which would be produced by an excess of tin in the state of protosalt, Mohr recommends that chlorine water should be added by drops to the mixture until a rod moistened with it and brought in contact with blue iodide of starch paper no longer removes the colour, the excess of protochloride of tin is then all converted into perchloride, and the titration with bichromate may proceed as usual. For the direct titration of iron by protochloride of tin see § 50.

It is absolutely necessary that the solution of ferridcyanide of potassium used as the indicator with bichromate should be free from ferrocyanide; and as a solution when kept for some little time becomes in some measure converted into the latter, it is best to use a freshly-prepared liquid, or at least to test the indicator with a persalt of iron previous to titration.

#### Preparation of the Decinormal Solution of Bichromate.

As 1 atom of bichromate of potash gives up 3 atoms of oxygen, it is necessary that  $\frac{1}{3}$ rd at. in grammes should be used for the litre as a normal solution, and  $\frac{1}{30}$ th for the decinormal; and as it is preferable on many accounts to use a dilute solution, the latter is the most convenient for general purposes.

According to the latest and most reliable researches, the

equivalent number of chromium is 26.24, and consequently that of bichromate of potash is 147.59; if therefore  $\frac{1}{30}$ th of this latter number = 4.919 Gm. be dissolved in a litre of water, the decinormal solution is obtained. On the grain system, 49.19 grains to 10,000 grains of water will give the same solution.

1 CC or 1 dm. of this solution is capable of yielding up  $\frac{1}{100.800}$  at. in grammes or grains of oxygen, and is therefore equivalent to the  $\frac{1}{100.800}$ th at. of any substance which takes up 1 atom of oxygen; but as 1 at. protoxide of iron requires only  $\frac{1}{2}$  at. oxygen to convert it into peroxide, each CC of bichromate is equal to  $\frac{1}{100.800}$  at. iron; and therefore, as in the case of permanganate, the atomic numbers used in the systematic calculations are doubled, so far as the protosalts are concerned.

#### Examples of Analysis.

0.7 Gm. of pure and dry double sulphate of iron and ammonia = 0.1 Gm. iron, was dissolved in about 2 oz. of water and titrated with decinormal bichromate, of which 17.85 CC were required; this multiplied by 0.0392 gave 0.699 Gm. instead of 0.7 Gm.

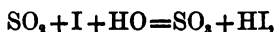
0.56 Gm. of iron wire required 99.8 CC = 0.5588 Gm.; as it is impossible to obtain iron wire perfectly pure, the loss is undoubtedly owing to the impurities.

If the bichromate solution should from any accidental cause be found not strictly of decinormal strength, the factor necessary for converting it must be found as in § 11.

As it is not at all an uncommon occurrence, in an analysis where no sign of the end of the reaction is visible in the solution itself, to overstep the exact point, it is advisable to have some method of bringing it into order again; this may be accomplished in the present case by adding a definite quantity of the double iron salt to the mixture, titrating afresh and deducting the proportional amount of bichromate from the total quantity required.

### IODINE AND HYPOSULPHITE OF SODA.

§ 45. The principle of this now beautiful and exact method of analysis was first discovered by Dupasquier, who used a solution of sulphurous acid instead of hyposulphite of soda. Bunsen improved his method considerably by ascertaining the sources of failure to which it was liable, and which consisted in the use of a too concentrated solution of sulphurous acid; the reaction between iodine and very dilute sulphurous acid may be represented by the formula:—



if the sulphurous acid is more concentrated, i.e., above 0.04 per cent. in a short time, the action is reversed, being

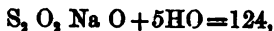


Under proper regulations, therefore, we see that free iodine converts sulphurous into sulphuric acid by decomposing water, the oxygen of which goes to the sulphurous, and produces sulphuric acid; the hydrogen is taken by the iodine, forming hydriodic acid.

There are great drawbacks, however, connected with the use of sulphurous acid; it very rapidly changes by keeping even in the most careful manner, so much so that a sample tested in the morning would very frequently need an examination in the afternoon; and as it must be exceedingly dilute, it necessitates the use of special vessels and burettes; taking all these things into account, therefore, the substitution of hyposulphite of soda is a great advantage, inasmuch as the end is secured quite as accurately without the trouble and insecurity connected with the sulphurous acid. The reaction in the case of hyposulphurous acid is as follows:—

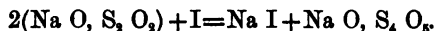


The composition of hyposulphite of soda is



and when brought in contact with a solution of iodine in iodide

of potassium, the hyposulphurous acid takes oxygen from the water, and the result is the production of tetrathionic and hydriodic acids in combination with soda.



In order to ascertain the end of the reaction in analysis by this method an indicator is necessary, and the most delicate and sensitive for the purpose is starch, which produces with free iodine the well known blue colour of iodide of starch.

### 1. Preparation of Starch Liquor.

1 part of clean arrowroot, potatoe, wheat, rice, sago, or other starch is first mixed smoothly with cold water into a paste, and about 150 or 200 times its weight of boiling water poured over it, and allowed to stand and settle, the clear liquor only is to be used as the indicator, of which a few drops only are necessary. As the liquor so prepared does not keep long, and is not near so sensitive when old, several methods have been devised for the purpose of preserving it; the best in my opinion is that proposed by Flückiger, which is as follows:—1 part of starch is well shaken and digested in a bottle with about 15 parts of a solution of chloride of calcium, containing half its weight of the salt; when the mixture appears slimy and fibrous, showing that the starch granules are broken, it is largely diluted with water, say to about 250 times its volume, it may then be allowed to settle, or is filtered, and the clear liquor saturated with common salt, then preserved in a cool place for use.

### 2. Preparation of the Decinormal Solution of Iodine.

Chemically pure iodine may be obtained by mixing commercial iodine with about one-fourth of its weight of iodide of potassium, and gently heating the mixture between two large watch-glasses or porcelain capsules, the lower one being placed upon a heated iron plate, the iodine sublimes in brilliant plates which are absolutely pure, the re-sublimed iodine of commerce is not

always free from chlorine, it is therefore sometimes necessary to prepare it specially by a second sublimation as described above.

The watch-glass or capsule containing the iodine is placed under the exsiccator to cool, and also to deprive it of any traces of watery vapour; then 12.7 Gm. ( $=\frac{1}{10}$  at.) accurately weighed, and together with about 18 Gm. of pure white iodide of potassium, dissolved in about a  $\frac{1}{2}$  litre of water, then diluted to exactly 1 litre. The same solution may be obtained by dissolving 127 grains of iodine, and 180 of iodide of potassium, in 10,000 grains of water, in either case the solution is strictly decinormal; the flask must not be heated in order to promote solution, and care must be taken that iodine vapours are not lost in the operation.

The solution is best preserved in stoppered bottles of about 5 or 6 oz. capacity which should be completely filled.

### 3. Decinormal Hyposulphite of Soda.

As 2 atoms of this salt are necessary to absorb 1 atom of iodine or oxygen, it is requisite that  $\frac{1}{2}$  at. in grammes of the pure salt should be contained in the litre, and as 124 is the equivalent number of the salt, 24.8 Gm. is the quantity to be weighed. As it is not difficult either to manufacture or procure pure hyposulphite of soda, this quantity, powdered and dried between blotting paper, may be weighed direct, and dissolved in a litre of distilled water, and then titrated with the iodine solution and a little starch liquor. If impure hyposulphite should have been used, or the sample not entirely free from accidental moisture, it will be necessary to find a factor by which to reduce it to decinormal strength, as described for alkalimetry, § 11, or the amount of impurity being known, a fresh quantity may be prepared of proper strength. It is advisable to preserve the solution in the dark.

Beside the decinormal iodine and hyposulphite, it is convenient in some cases to use centinormal solutions, which can

readily be prepared by diluting 100 CC. of each decinormal solution to 1 litre.

In using the iodine solution, Mohr's burette may be employed, but care must be taken that the solution is not left in it for any length of time, as decomposition slowly takes place, and the tube becomes hard. Gay Lussac's, or the bulb burette, are on this account preferable.

#### 4. Preparation for the Analytical Process.

There are a great variety of substances containing oxygen, which, when boiled with hydrochloric acid, yield chlorine, equivalent to the whole or a part only of the oxygen they contain, according to circumstances. Upon this fact are based the variety of analyses which may be accomplished by means of iodine and hyposulphite of soda; the chlorine so evolved, however, is not itself estimated, but is conveyed by means of a suitable apparatus into a solution of iodide of potassium, thereby liberating an equivalent quantity of iodine. This latter body is then estimated by hyposulphite of soda; the quantity so found is therefore a measure of the oxygen existing in the original substance, and consequently a measure of the substance itself. It seems a very roundabout method, and one would imagine it could scarcely lead to accurate results; nevertheless, without exaggeration, it may be said to be the most exact in the whole range of volumetric analyses, far outstripping any process of analysis by weight.

The apparatus used for distilling the substances, and conveying the liberated chlorine into the alkaline iodide, may possess a variety of forms, the most serviceable, however, being the three kinds devised respectively by Bunsen, Fresenius, and Mohr.

Bunsen's consists of a small flask to contain the mixture for distillation, connected by a stout piece of vulcanized tubing with a long bent tube, which is carried into the solution of iodide contained in an inverted retort, the neck of the latter having a tolerably large bulb blown midway, so that when the

chlorine is all evolved from the mixture, and hydrochloric acid gas begins to distil, the rapid condensation which ensues may not cause the liquid to rush back to the flask, and so spoil the operation; this unavoidable regurgitation is a great nuisance, and in order to prevent the entrance of the liquid into the bent tube, Bunsen contrived a little self-acting valve, which consists of a very light glass bulb with a stalk, (very like the large headed ornamental pins used by ladies for their hair,) this presents no hindrance to the evolution of the gas during the distillation, but when the liquid attempts to enter, the bulb is forced up to the end of the delivery tube, so as to close

the entrance; a drawing of the entire apparatus may be seen in most treatises on chemical analysis.

The apparatus contrived by Fresenius differs from Bunsen's only in having two large bulbs blown in the neck of the retort and one in the bent delivery tube, in this case the glass valve is not necessary.

Mohr's apparatus is shewn in Fig. 16, and



Fig. 16.



is in my opinion preferable to either of the foregoing, on account of its simplicity of construction and more accurate working.

The distilling flask is of about 2 oz. capacity, and is fitted with a cork soaked to saturation in melted paraffin, through the cork the delivery tube containing one bulb passes, and is again passed through a common cork, fitted loosely into a stout tube about 12 or 13 inches long and 1 inch wide, closed at one end like a test tube; this tube, containing the alkaline iodide, is placed in an ordinary hydrometer glass, about twelve inches high, and surrounded by cold water; the delivery tube is drawn out to a fine point, and reaches nearly to the bottom of the condenser. No support or clamp is necessary, as the tall hydrometer glass keeps everything in position. The substance to be distilled is put into the flask and covered with strong hydrochloric acid, the condenser supplied with a sufficient quantity of iodide solution, and the apparatus put together tightly; either an argand or common spirit lamp, or gas, may be used for heating the flask, but the flame must be manageable, so that the boiling can be regulated at pleasure; in the case of the common spirit lamp, it may be held in the hand, and applied or withdrawn according to the necessities of the case; the argand spirit or gas lamp can of course be regulated by the usual arrangements for the purpose. If the iodine liberated by the chlorine evolved, should be more than will remain in solution, the cork of the condensing tube must be lifted, and more solution added. When the operation is judged to be at an end, the apparatus is disconnected, and the delivery tube washed out into the iodide solution, which is then emptied into a beaker or flask, and preserved for analysis, a little fresh iodide solution is put into the condenser, the apparatus again put together, and a second distillation commenced, and continued for a minute or so, to collect every trace of free chlorine present. This second operation is only necessary as a safeguard in case the first should not have been complete.

The solutions are then mixed together and titrated in the manner presently to be described.

The solution of iodide of potassium may conveniently be made of such a strength that  $\frac{1}{10}$  atom or 33.2 Gm. is contained in the litre. One cubic centimeter will then be sufficient to absorb the quantity of free iodine, representing 1 per cent. of oxygen in the substance analysed, supposing it to be weighed in system. In examining peroxide of manganese for instance, 0.436 Gm. or 4.36 grn. would be used, and supposing the percentage of peroxide to be about 60, 60 CC or dm. of iodide solution would be sufficient to absorb the chlorine and keep in solution the iodine liberated by the process; it is advisable, however, to have an excess of iodide, and, therefore, in this case, about 70 CC or dm. should be used. A solution of indefinite strength will answer as well, so long as enough is used to absorb all the iodine.

The process of distillation above described is troublesome, and therefore it is advisable to avoid it where possible. There are a great number of substances which, by mere digestion with hydrochloric acid and iodide of potassium at an elevated temperature, undergo decomposition quite as completely as by distillation. For this purpose a strong bottle with a very accurately ground stopper is necessary; and as the ordinary stoppered bottles of commerce are not sufficiently tight, it is better to regrind the stopper with a little *very fine* emery and water. It must then be tested by tying the stopper tightly down and immersing in hot water, if any bubbles of air find their way through the stopper the bottle is useless. The capacity may vary from 1 to 5 or 6 oz., according to the necessities of the case.

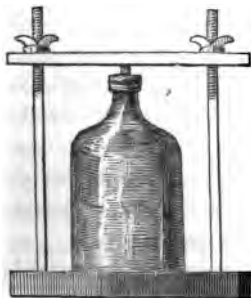


Fig. 17.

The stopper may be secured by fine copper binding wire, or a kind of clamp contrived by Mohr may be used, as shewn in Fig. 17; by means of the thumb screws the pressure upon the stopper may be increased to almost any extent.

The substance to be examined, if in powder, is put into the bottle with pure flint pebbles or small garnets, so as to divide it better, and a sufficient quantity of *saturated* solution of iodide of potassium and pure hydrochloric acid added, the stopper is then inserted, fastened down, and the bottle placed in a saucepan of water with a little tow, or other similar substance, to keep the glass from touching the bottom, and the water then made to boil by a gas flame or hot plate as may be most convenient; when the decomposition is complete the bottle is removed, allowed to cool somewhat, then placed in cold water, and, after being shaken, is opened, emptied into a beaker, and diluted by the washings for titration. The salts of chloric, iodic, bromic, and chromic acids, together with many other compounds, may be as effectually decomposed by digestion as by distillation.

#### The Analytical Process.

The free iodine existing in solution with iodide of potassium, as just described is not estimated direct by the hyposulphite, but by a residual method, that is to say an excessive quantity of hyposulphite is allowed to flow from a large burette, graduated in  $\frac{1}{4}$  CC until the colour of the iodine is removed, the excess of hyposulphite is then estimated by the addition of starch liquor and decinormal iodine, the latter being delivered from a small burette graduated in  $\frac{1}{10}$  CC until the blue colour appears; the quantity so required is deducted from that of the hyposulphite, and the analysis calculated in the systematic way.

Reducing substances, such as sulphurous, hyposulphurous, and hydrosulphuric acid, alkaline arsenites, &c., are, of course, titrated direct with the iodine solution and starch.

The iodide of potassium used in the various analyses must be absolutely free from iodate of potash and free iodine.

**ARSENIOUS ACID AND IODINE.**

§ 46. THE principle upon which this method of analysis is based is the fact that when arsenious acid is brought in contact with iodine in the presence of water and free alkali, it is converted into arsenic acid, the reaction being—



The alkali must be in sufficient quantity to combine with the hydriodic acid set free, and it is necessary that it should exist in the state of carbonate, as pure alkalies interfere with the colour of the blue iodide of starch used as indicator.

If, therefore, a solution of arsenious acid containing starch is titrated with a solution of iodine in the presence of carbonate of soda, the blue colour does not occur until all the arsenious acid is oxidised into arsenic acid; in like manner, a standard solution of arsenious acid may be used for the estimation of iodine or other bodies which possess the power of oxidising it.

The chief value, however, of this method is found in the estimation of free chlorine existing in the so-called chloride of lime, chlorine water, hypochlorites of lime, soda, &c., in solution, generally included under the term chlorimetry.

**1. Preparation of the Decinormal Solutions of Iodine  
and Arsenite of Soda.**

The iodine solution is the same as described in § 45, 2, containing 12·7 Gm. in the litre.

The corresponding solution of arsenite of soda is prepared by dissolving 4·95 Gm. of the purest sublimed arsenious acid, free from sulphide, in about a  $\frac{1}{4}$  litre of distilled water in a flask, with about 25 Gm. of the purest crystallized carbonate of soda, free from sulphide, hyposulphite, or sulphite of sodium. It is necessary that the acid should be in powder, and the mixture needs boiling and shaking for some time in order to complete

the solution; when this is accomplished the mixture is diluted somewhat, and filtered into the litre measure, the filter well washed, and the solution then made up to the litre. The equivalent number of arsenious acid being 99, and 1 atom absorbing 2 at. of oxygen, the  $\frac{1}{10}$  part or 4.95 Gm. is necessary to form the decinormal solution.

In order to test this solution 10 CC are put into a beaker glass with a little starch liquor, and the iodine solution allowed to flow in from a burette, graduated in  $\frac{1}{10}$  CC, until the blue colour appears, if exactly 10 CC are required the solution is strictly decinormal, if otherwise, the necessary factor must be found for converting it to that strength.

Starch liquor, however, cannot be used for the direct estimation of free chlorine, consequently resort must be had to an external indicator, and this is very conveniently found in iodide of starch paper, which is best prepared by mixing a portion of the starch liquor described in § 45, 1, with a few drops of solution of iodide of potassium on a plate, and soaking strips of pure filtering paper therein; the paper so prepared is used in the damp state, which is far more sensitive than the dried paper prepared according to Penot's plan.

## 2. The Analytical Process.

In all cases the chlorine to be estimated must exist in an alkaline solution. In the case of chloride of lime this is already accomplished by the caustic lime which invariably exists in the compound.

The substance being brought under the burette containing the arsenious acid solution, it is suffered to flow until a drop of the mixture taken out with a glass rod and brought in contact with the prepared paper, no longer produces a blue spot. As the colour becomes gradually lighter towards the end of the process, it is not difficult to hit the exact point, should it,

however, by any accident be overstepped, starch liquor may be added to the mixture, and decinormal iodine solutions added until the blue colour is produced; the quantity so used is then deducted from the total arsenic solution.

Examples. 50 CC of chlorine water were mixed with solution of carbonate of soda, and brought under the arsenic burette, and 20 CC of solution added, on touching the prepared paper with the mixture no colour was produced, consequently the quantity used was too great; starch liquor was therefore added and decinormal iodine, of which 3.2 CC were required to produce the blue colour. This gave 16.8 CC of arsenic solution, which multiplied by 0.003546 gave 0.05857 Gm. Cl in the 50 CC. A second operation with the same water required 16.8 CC of arsenic solution direct, before the end of the reaction with iodized starch paper was reached.

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### BODIES SUBJECT TO DETERMINATION BY OXIDISING OR REDUCING AGENTS.

Under this head are included all those substances which may, with accuracy and rapidity, be analysed by the foregoing methods.

The names of the discoverers of the various processes will be given, and also examples of their accuracy where practicable.

#### IRON. Fe—28.

#### § 47.

Substance.	Formula.	Atomic Weight	Quantity to be weighed so that 1 CC or 1 dm. of decinormal solution = 1 per cent. of substance.	$\frac{N}{10}$ Factor.
Metallic Iron (2 atoms)	2Fe	56	0.56 Gm., or 5.6 grn.	0.0056, or 0.056
Protoxide of Iron (2 at.)	2FeO	72	0.72 Gm., or 7.20 grn.	0.0072, or 0.072
Peroxide of Iron (1 at.)	Fe <sub>2</sub> O <sub>3</sub>	80	0.80 Gm., or 8.00 grn.	0.0080, or 0.080
Carbonate of Iron (2 at.)	2(FeO, CO <sup>2</sup> )	116	1.16 Gm., or 11.60 grn.	0.0116, or 0.116
Protosulphate of Iron (2 at.)	2(FeO, SO <sub>3</sub> + 7HO)	278	2.78 Gm., or 27.8 grn.	0.0278, or 0.278
Double Sulphate of Iron and Ammonia (2 at.)	2(FeO + 2SO <sub>3</sub> + NH <sub>4</sub> O + 6HO)	392	3.92 Gm., or 39.20 grn.	0.0392, or 0.392

**Factors.**

Metallic iron	×	1.2857	=	FeO
" "	×	1.4286	=	Fe <sub>2</sub> O <sub>3</sub>
" "	×	2.0714	=	FeO.CO <sub>2</sub>
" "	×	4.9643	=	FeO.SO <sub>3</sub> +7HO
" "	×	7.0000	=	FeO.2SO <sub>3</sub> +NH <sub>4</sub> O+6HO

In the analysis of iron ores it is very often necessary to determine not only the total amount of iron but also the state in which it exists; for instance, magnetic iron ore consists of a mixture of the two oxides in tolerably definite proportions, and it is sometimes advisable to know the quantities of each.

In order to prevent, therefore, the further oxidation of the protoxide and so leading to false results, the little flask apparatus, (Fig. 18,) adapted by Mohr is highly recommendable.

The left hand flask contains the weighed ore in a finely powdered state, to which tolerably strong hydrochloric acid

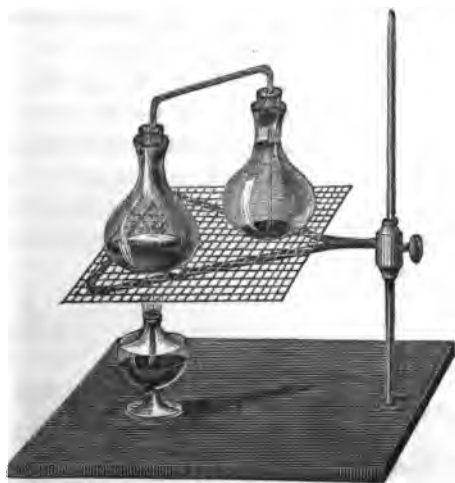


Fig. 18.

is added; the other flask contains distilled water only; the tube from the first flask entering to the bottom of the second. When the ore is ready in the flask and the tubes fitted, hydrochloric acid is poured in and a few grains of bicarbonate of



soda added to produce a flow of carbonic acid, the air of the flask is thus dispelled, and as the acid dissolves the ore, the gases evolved drive out in turn the carbonic acid which is partly absorbed by the water in the second flask. When the ore is all dissolved and the lamp removed, the water immediately rushes out of the second flask into the first, diluting and cooling the solution of ore, so that in the majority of cases it is ready for immediate titration; if not sufficiently cool or dilute, a sufficient quantity of boiled and cooled distilled water is added. When the total amount of iron present in any sample of ore has to be determined, it is necessary to reduce any peroxide present to the state of protoxide by zinc, this must be free from iron, or at least if it contain iron the quantity must be known so that a deduction may be made in the analysis; the best vessel in which to make the reduction is the flask described for the solution of metallic iron in titrating permanganate.

The end of the process may be known either by the disappearance of the colour of the peroxide, or by testing with a small glass rod dipped in sulphocyanide of potassium, in which case no red colour must appear. The zinc is best added in small fragments, none of which should be left undissolved when the titration takes place. For the method of reduction by protochloride of tin, see § 44.

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## TECHNICAL EXAMINATION OF IRON ORES, &c.

### Magnetic Iron Ore.

§ 48. THE protoxide is determined first by means of the apparatus, Fig. 16, or instead of the two flasks one only may be used, or a wide and long test tube—in either case a cork containing a small bent tube is inserted; the ore is put into the vessel in a state of fine powder, strong hydrochloric acid added,

together with a few grains of bicarbonate of soda, and the bent tube dipped under the surface of some cold distilled water; heat is now applied gently with the lamp until the ore is dissolved, the heat is then removed, and the water rushes into the tube, diluting and cooling the solution. It may then be poured out into a larger quantity of water, if necessary, and titrated with bichromate of potash.

Example. 0.5 Gm. of ore was treated as above, and required 19.5 CC of  $\frac{N}{10}$  bichromate, which multiplied by 0.0056 gave 0.1092 Gm. iron = 0.1404 Gm. protoxide = 28.08 per cent.

The peroxide was now found by reducing 0.5 Gm. of the same ore with zinc, and estimating the total iron present, the quantity of bichromate required was—

$$\begin{array}{rcl}
 59 \text{ CC } \frac{N}{10} & = & 0.3304 \text{ Gm. total Fe} \\
 \text{Deduct...} & 0.1092 & \text{,, as protox.} \\
 \hline
 \text{Leaving} & 0.2212 & \text{,, as perox.}
 \end{array}$$

The result of the analysis is, therefore,—

Protoxide of Iron .....	28.08 per cent.
Peroxide of ditto.....	63.20 „
Gangue, &c.....	8.72 „
	<hr/>
	100.00
	<hr/>

#### Spathose Iron Ore.

The total amount of protoxide of iron in this carbonate is ascertained direct by solution in hydrochloric acid in a test tube, with cork and bent tube dipped into water to prevent oxidation; or as the carbonic acid evolved is generally sufficient to expel all air, the dipping under water may be dispensed with. Should the ore be very impure, zinc may have to be added in order to insure the reduction of all the iron present.

As the ore contains in most cases the carbonates of manganese, lime, and magnesia, these may all be determined, together with the iron, as follows—

A weighed portion of ore is brought into solution in hydrochloric acid, and filtered, if necessary, to separate insoluble silicious matter.

The solution is then boiled, with a few drops of nitric acid to peroxidise the iron, diluted, and carbonate of soda added in sufficient quantity to precipitate the oxide of iron, then acetate of soda, and the whole boiled that the precipitate may become somewhat dense and separate from the liquid; filter, and if necessary, reduce the oxide of iron after careful washing, with zinc, and determine with bichromate or permanganate.

The filtrate containing the other bases is treated with hypochlorite of soda, covered and set aside for 24 hours in order to precipitate the manganese as hydrated oxide, which is collected and titrated as in § 55, 4.

The filtrate from the last is mixed with oxalate of ammonia to precipitate the lime, which is estimated by permanganate, as in § 60, 1.

The filtrate from the lime contains the magnesia, which may be precipitated with phosphate of soda and ammonia, and the precipitate weighed as usual or titrated with uranium solution, as in § 78, 1, see also § 38.

Red and brown hematites can be examined in a similar manner to the foregoing.

#### Chrome Iron Ore.

This material, which is mainly derived from America, is of great commercial importance, as being the source of bichromate of potash.

The ore varies considerably in quality, some samples being very rich, while others are very poor in chromium. In the case of those tolerably free from gangue, the sample is to be first of

all brought into *very fine* powder. About 10 grains are rubbed tolerably fine in a steel mortar, then finished fractionally in an agate mortar; 0.5 Gm. is then carefully weighed, and mixed with about 3 Gm. of a mixture of dried carbonate of potash and soda, and fused strongly for twenty minutes in a platinum crucible. The mass is then cooled, lixiviated with warm water, filtered, and the filtrate titrated for chromium as in § 65, 1.

The oxide of iron remaining on the filter is boiled with hydrochloric acid, diluted and titrated with bichromate of potash.

When the ore contains a larger proportion of silicious or earthy gangue, or much other impurity, it may be necessary to adopt the following method, modified somewhat from O'Neill's process, described in "Chem. News," April 12th, 1862.

The very finely powdered ore is fused with ten times its weight of bisulphate of potash for twenty minutes, taking care that it does not rise over the edge of the platinum crucible; when the fusion is complete, the molten mass is caused to flow over the sides of the crucible, so as to prevent the formation of a solid lump, and the crucible set aside to cool. The mass is then transferred to a porcelain dish, and lixiviated with warm water until entirely dissolved; no black residue must occur, otherwise the ore is not completely decomposed; carbonate of soda is then added to the liquid until it is strongly alkaline; it is then brought on a filter, washed slightly, and the filter dried. When perfectly dry, the precipitate is detached from the filter as much as possible; the filter burned separately; the ashes and precipitate mixed with about twelve times the weight of the original ore, of a mixture of two parts chlorate of potash and three parts carbonate of soda, and fused in a platinum crucible for twenty minutes or so; the resulting mass is then treated with boiling water, filtered, and the filtrate titrated for chromic acid as before.

The oxide of iron remaining on the filter is titrated, if required, with bichromate of potash.

**ESTIMATION OF THE PERCENTAGE OF PURE IRON IN STEEL,  
CAST AND WROUGHT IRON, SPIEGELEISEN, &c.**

**Mohr's Method.**

§ 49. INSTEAD of the hitherto common method of separately estimating the impurities in samples of manufactured iron and steel, this process is adapted to the delicate estimation of the iron itself, and is similar in principle to the assay of silver by Gay Lussac's method, that is to say, the analysis is so arranged that the greatest accuracy shall be secured.

The standard solutions of bichromate of potash, of which there are two, are so prepared that 100 CC or dm. of the first will exactly convert respectively 1 Gm. or 10 grains of iron into peroxide, the second, or decimal solution, is one-tenth the strength of the first.

The solution of bichromate No. 1 is prepared by dissolving 8·785 Gm. of the pure salt in 1 litre, or 87·85 grn. in 10,000 grains of distilled water at 62° Fahr. The decimal solution No. 2 is made by taking 100 CC of No. 1 and diluting it to 1 litre, or 100 decems to 10,000 grains, therefore—

100 CC or dm. of No. 1=0·01 Gm. or 0·1 grn. iron.

100 CC or dm. of No. 2=0·001 Gm. or 0·01 grn. ditto.

**The Analytical Process.**

The sample of iron to be examined is reduced to powder in a hardened steel mortar, or if in the form of wire, or in a soft state, cut into small pieces, and exactly 1·050 Gm. or 10·50 grn. weighed off; this is brought into a long and wide test tube, or small flask, fitted loosely with a cork, and dissolved in pure hydrochloric or sulphuric acid. When the solution is accomplished, 100 CC or dm. of bichromate solution No. 1 (containing 0·8785 Gm. or 8·758 grn. of bichromate, which is exactly

sufficient to peroxidise respectively 1 Gm. or 10 grn. of pure iron) is added ; the decimal solution is then added from a small burette, until a drop of the mixture, brought in contact with red prussiate of potash, no longer produces a blue colour ; the analysis is then calculated in the usual way.

Examples : 1.05 Gm. of Bessemer's steel was dissolved in pure sulphuric acid, 100 CC bichromate No. 1 added, and afterward 39 CC of No. 2 required for complete oxidation ; consequently there were 1.039 Gm. of pure iron contained in the 1.050 Gm. taken for analysis ; this is equal to 989.4 parts per thousand, or 98.94 per cent.

Instead of the empirical solutions here described, the ordinary decinormal and centinormal solutions of bichromate may be employed with equal accuracy. As 100 CC of decinormal solution is equal to 0.56 Gm. of pure iron, it is necessary that somewhat more than this quantity of the sample should be weighed, say 0.58 or 0.60 Gm. 100 CC of decinormal solution then added, and the analysis completed with the centinormal solution.

This system of analysis, in order to express directly the percentage of iron in a given sample, can be arranged in the following manner. A solution of protoxide of iron is prepared by dissolving 7 Gm. of the double sulphate of iron and ammonia in distilled water, adding a considerable quantity, say 50 CC, of pure sulphuric acid, and diluting to 1 litre. 1 CC of this solution contains 1 milligramme of iron.

1 Gm. of the sample of iron is dissolved, and 100 CC of bichromate solution No. 1 added ; the excess is then ascertained by the iron solution described above ; the quantity so used deducted from the 100 CC of bichromate will give the percentage of pure iron direct ; the objection to this method is that the iron solution is subject to oxidation.

## DIRECT TITRATION OF IRON BY PROTOCHLORIDE OF TIN.

§ 50. THE reduction of peroxide of iron to the state of protoxide by this reagent has been previously referred to, and it will be readily seen that the principle involved in the reaction can be made available for a direct estimation of iron, being, in fact, simply a reversion of the ordinary process by permanganate and bichromate. In the case of these two reagents, the amount of oxygen *given up* by them is the measure of the quantity of iron, whereas with protochloride of tin, it is the amount *taken up* by it that answers the same purpose.

Fresenius (in his "Zeitschrift für Analytische Chemie," part 1, page 26) has recorded a series of experiments made on the weak points of this process, and gives it as his opinion that it is most accurate and reliable with proper care, without which, of course, no analytical process whatever is worth anything. The summary of his paper is as follows:—

a. A solution of peroxide of iron of known strength is first prepared, by dissolving 10.03 Gm. fine pianoforte wire (=10 Gm. pure iron) in pure hydrochloric acid, adding chlorate of potash to complete oxidation; boiling till the excess of chlorine is removed, and diluting the solution to 1 litre.

b. A clear solution of protochloride of tin, of such strength that about equal volumes of it and the iron solution are required for the complete reaction.

c. A solution of iodine in iodide of potassium, containing about 0.005 Gm. iodine in 1 CC, (if the operator has the ordinary decinormal iodine solution at hand, it is equally applicable.) The operations are as follows:—

1. 1 or 2 CC of the tin solution are put into a beaker with a little starch liquor, and the iodine solution added from a burette till the blue colour occurs; the quantity is recorded.

2. 10 CC of the iron solution=0.1 Gm. iron, are put into a small flask with a little hydrochloric acid, and heated to

gentle boiling, (preferably on a hot plate), the tin solution is then allowed to flow in from a burette until the yellow colour of the solution is nearly destroyed, it is then added drop by drop, waiting after each addition until the colour is completely gone and the reduction ended. If this is carefully managed there need be no more tin solution added than is actually required; however, to guard against any error in this respect, the solution is cooled, a little starch liquor added, and the iodine solution added by drops until a permanent blue colour is obtained. As the strength of the iodine solution compared with the tin has been found in 1, the excess of tin solution corresponding to the quantity used is deducted from the original quantity, so that by this means the volume of tin solution corresponding to 0.1 Gm. iron is found.

The operator is, therefore, now in a position to estimate any unknown quantity of iron which may exist, in a given solution, in the state of peroxide, by means of the solution of tin.

If the iron should exist partly or wholly in the state of protoxide, it must be oxidised by the addition of chlorate of potash, and boiling to dissipate the excess of chlorine, as described in 2.

Example: 10 CC of iron solution, containing 0.1 Gm. iron, required 15 CC of tin solution.

A solution, containing an unknown quantity of iron, was then taken for analysis, which required 12 CC, consequently a rule of three sum gave the proportion of iron as follows:—

$$15 : 0.1 \text{ Gm.} :: 12 : 0.08 \text{ Gm.}$$

It must be remembered that the solution of tin is not permanent, consequently it must be tested every day afresh. Two conditions are necessary in order to insure accurate results.

1st. The iron solution must be tolerably concentrated, since the end of the reduction by loss of colour is more distinct; and, further, the dilution of the liquid to any extent interferes with the quantity of tin solution necessary to effect the reduction.



Fresenius found that by diluting the 10 CC of iron solution with 30 CC of distilled water,  $\frac{1}{10}$  of a CC more was required than in the concentrated state. This is, however, always the case with protochloride of tin in acid solution, and constitutes the weak point in Streng's method of analysis by its means; it would seem that dilution either predisposed it to rapid oxidation, or that water had the power within itself to communicate a certain proportion of oxygen to it.

2nd. The addition of the tin solution to the iron must be so regulated that only a very small quantity of iodine is necessary to estimate the excess—if this is not done another source of error steps in, namely, the influence which dilution, on the one hand, or the presence of great or small quantities of hydrochloric acid on the other, are known to exercise over this reaction; practically it was found that where the addition of tin, to the somewhat concentrated iron solution, was cautiously made so that the colour was just discharged, the mixture then rapidly cooled, starch added and iodine till blue, that the estimation was as reliable as by any other method.

The following examples are from Fresenius.

The standard iron solution contained 10 Gm. in the litre; 10 CC were therefore equal to 0.1 Gm. iron. 1 CC tin solution required 3.62 CC iodine.

Exp. 1. 9.97 CC of the above iron solution required 11.6 CC tin solution and 1.23 CC iodine.

Exp. 2. 9.87 CC iron solution required 11.26 CC tin and 0.44 CC iodine. Calculated for 0.1 Gm. iron, the above experiments shew that—

1	=	11.294	CC tin solution
2	=	11.287	” ”
Mean		11.2905	” ”

3.8204 Gm. brown hematite ore was heated with concentrated hydrochloric acid until decomposed, then diluted somewhat, filtered, and the solution made up to 500 CC.

Exp. 1. 100 CC required 43·69 CC tin solution and 0·26 CC iodine.

Exp. 2. 100 CC required 44·15 CC tin and 2·12 CC iodine, therefore,—

1	=	43·62	CC	tin	solution
2	=	43·57	"	"	
Mean		43·60	"	"	

The following equation expresses the result.

$11\cdot2905 \text{ SnCl} : 0\cdot1 \text{ Fe} :: 43\cdot60 : x = 0\cdot3862 \text{ Gm. iron in 100 CC, or } 50\cdot54 \text{ per cent. of iron in the ore.}$

A determination of the iron, in the same sample of ore, by permanganate, executed with the greatest care, gave 50·58 per cent.

The tin solution is best prepared by placing fragments of pure tin at the bottom of a beaker, laying a small platinum crucible or cover upon them, and covering the whole with equal parts of pure hydrochloric acid and water: a large watch glass or porcelain capsule should be placed on the top of the beaker to exclude air and prevent loss by spirting.

The contact of the platinum with the tin sets up a galvanic current which materially hastens the solution of the tin without at all affecting the platinum; when the acid is all saturated, it may be poured off and fresh added until sufficient solution has been obtained. The whole, freely acidified and diluted to a convenient strength, should be placed in a well stoppered bottle, with a few fragments of tin; its strength, which is constantly lessening to a slight extent, must be found before using it.

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## TITRATION OF IRON BY HYPOSULPHITE OF SODA.

§ 51. PROFESSOR SCHERER first suggested the direct titration of iron by hyposulphite of soda, which latter was added to a solution of the perchloride of iron until no further violet colour was produced. This was found by many to be inexact, but Kremer, (*Journ. f. Pract. Chem.*, 84, 339,) has made a series of careful experiments, the result of which is that the following modified method can be highly recommended.

The reaction which takes place between hyposulphite of soda and perchloride of iron is such that 2 eq. of the former with 1 eq. of the latter, produce 2 eq. protochloride of iron, 1 eq. tetrathionate of soda, and 1 eq. chloride of sodium. The hyposulphite, which may conveniently be of  $\frac{N}{10}$  strength, is added in excess, and its amount determined by  $\frac{N}{10}$  iodine and starch liquor.

Process. The iron solution, containing not more than 1 per cent. of metal, which must exist in the state of perchloride without any excess of oxidising material, (best obtained by adding concentrated permanganate of potash until the red colour is produced, then boiling till both that and any free chlorine is expelled), is moderately acidified with hydrochloric acid, acetate of soda added till the mixture is red, then dilute hydrochloric acid until the red colour disappears; then diluted till the iron amounts to  $\frac{1}{4}$  or  $\frac{1}{2}$  per cent., and  $\frac{N}{10}$  hyposulphite added in excess, best known by throwing in a particle of sulphocyanide of potassium after the violet colour produced by the hyposulphite has disappeared—if any red colour occurs, more hyposulphite must be added. Starch liquor and  $\frac{N}{10}$  iodine are then used to ascertain the excess of hyposulphite; each CC of the latter is equal to 0.0056 iron. A mean of several experiments gave 100.06 Fe, instead of 100.

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## COPPER. Cu=31.7.

## § 52.

Substance.	Formula.	Atomic Weight	Quantity to be weighed so that 1 CC or 1 dm. of decinormal solution=1 per cent. of substance.	N TO Factor.
Copper (2 atoms) ...	2 Cu	63.4	0.634 Gm., or 6.34 grn.	0.00634, or 0.0634
Protoxide of Copper (1 at.)	Cu <sub>2</sub> O	71.4	0.714 Gm., or 7.14 grn.	0.00714, or 0.0714
Oxide of Copper (2 at.)	2Cu O	79.4	0.794 Gm., or 7.94 grn.	0.00794, or 0.0794
Crystallized Sulphate of Copper (2 at.)	2(Cu O, SO <sub>3</sub> +5H <sub>2</sub> O)	249.4	2.494 Gm., or 24.94 grn.	0.02494, or 0.2494

Factors for converting the quantity of Iron represented by  
Permanganate or Bichromate into Copper.

Iron  $\times$  1.1314 = Copper  
 „  $\times$  1.4171 = Oxide of ditto  
 „  $\times$  4.453 = Crystallized sulphate of ditto

Double Iron Salt  $\times$  0.16163 = Copper  
 „ „  $\times$  0.2024 = Oxide ditto  
 „ „  $\times$  0.6361 = Crystallized sulphate

So many methods have been proposed for the volumetric estimation of copper that the analyst is bewildered by their number and hardly knows upon which to depend.

My own opinion is that in the majority of cases it is safer and less troublesome to estimate the metal by weight; there are, however, instances where volumetric methods can be applied with advantage, and the following processes are chosen as the best.

1. **Method of separating Copper from any of its Ores or Residues in a pure Metallic state, so that it may be weighed direct or estimated by Volumetric methods.—(Mohr, somewhat modified.)**

The substance must be brought into very fine powder, particularly if it contain sulphur, and about 5 Gm. of it weighed, placed in a deep porcelain crucible or capsule about 4 in. in diameter, and covered with a concentrated mixture of nitric and sulphuric acids and water, added cautiously; a larger quantity of nitric acid is necessary when sulphur is present, (as in pyrites), than in other cases; a watch glass or another capsule is placed upon the top of that containing the mixture so as to prevent loss by spirting—preferably a large watch glass with a hole drilled in the middle. Heat is then applied to boiling and continued till the mass is nearly dry, the cover is then removed, and if not washed clean by the steam produced in the operation itself, is washed with a small quantity of water into the mass which is again evaporated to dryness, the heat is then increased until all acid vapours are expelled, and the capsule set aside to cool. In the case of pyrites the heat must be continued long enough to burn the sulphur off, the capsule may then be slightly cooled and nitric acid again added, and the burning repeated; in certain cases this may be necessary a third time in order to oxidise all sulphur and extraneous matter.

By this treatment the copper is obtained as sulphate, the iron mostly as insoluble basic sulphate, lead as insoluble sulphate, antimony and tin also insoluble, zinc, cobalt, and nickel are of no consequence in the following treatment. The cold residue is covered with water and boiled till all soluble matter is extracted, then filtered through a small filter into a weighed platinum dish, the residue being washed clean with boiling water, the dish, with its contents, is then placed on the water-bath or over a small spirit lamp, gently heated, acidified with hydrochloric acid, and a small lump of pure zinc added to

reduce the copper to the metallic state ; there must be sufficient acid to produce a distinct evolution of hydrogen, and the dish covered with a watch glass to prevent loss of liquid by spiriting, the glass afterward being rinsed into the liquid. The end of the reduction is best known by taking a drop of the supernatant liquid out with a glass rod, and touching the surface of some acidulated sulphuretted hydrogen water contained in a small white capsule, if no brown colour is produced, the reduction is ended, and any undissolved zinc can either be removed mechanically with a pair of forceps, taking care to free it from any adhering copper, or dissolved by the addition of fresh acid. The precipitated copper, if pure and clean, will possess a rose red colour, it must be quickly washed with boiling water to free it from acid—the first washings should be poured off into a beaker and allowed to settle by themselves, as small particles of copper may accidentally be contained in them, if so, they must be washed clean and added to the platinum dish. Air should not be admitted to the metallic copper while the acid is present to any great extent. When the washings no longer affect litmus paper, the dish should be placed in an air bath, heated to 212° or 215° Fahr., and dried till the weight is constant—the increase in weight is pure copper. A water-bath may be used for drying the copper, in which case it is preferable to wash it first with strong alcohol.

Instead of a platinum dish porcelain or glass will answer, but more time is required, as there is no galvanic action to hasten the decomposition as with the platinum ; in this case the deposited copper is not attached to the sides or bottom of the vessel.

Instead of drying and weighing the copper it can be dissolved and estimated by Fleitmann's process, § 52, 3, or the following modification may be adopted. The solution obtained by digesting the residue of the first operation in water, invariably contains iron, whenever that metal is present in the original substance ; in order to remove it, therefore, the neutral and

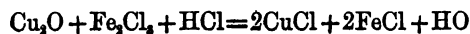
concentrated solution is boiled with a tolerable quantity of acetate of soda, the insoluble iron precipitate filtered off, washed with boiling water containing acetate of soda, and the copper solution, which must not be too dilute, titrated by De Haen's method, with hyposulphite of soda; or in the absence of manganese, cobalt, nickel, arsenic, mercury, silver, and zinc, the solution, without removing the iron, may be titrated direct with cyanide of potassium as in § 52, 5, using the precautions there mentioned.

Examples of the accuracy with which copper may be separated from ores and other compounds by precipitation with zinc:—

1 Gm. pure metallic copper was mixed with 0.5 Gm. each of the following substances, either as metals or salts, viz.:—gold, silver, platinum, tin, lead, iron, zinc, nickel, cobalt, bismuth, arsenic, uranium, mercury, molybdenum, antimony, sulphur, silica, and phosphate of lime. The whole was treated with nitric and sulphuric acids as previously described, and the residue, after one ignition, lixiviated with water, filtered off, and treated with hydrochloric acid to remove silver, then after filtration, zinc and hydrochloric acid added in a large platinum dish. The yield of pure copper was 0.996 Gm.; without recording any further experiments in detail, it may suffice to say that in more than twenty determinations of copper in various combinations, the mean results obtained were 99.7 instead of 100.

## 2. Schwarz's method, (results tolerably accurate.)

This process is based upon the fact that grape sugar precipitates protoxide of copper from an alkaline solution of the metal containing tartaric acid, the protoxide so obtained is collected and mixed with perchloride of iron and hydrochloric acid—the result is the following decomposition:—



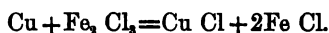
Each equivalent of copper reduces an equivalent of perchloride of iron to protochloride, which is estimated by permanganate. The iron so obtained is calculated into copper by the requisite factor.

Process: The weighed substance is brought into solution by nitric or sulphuric acid or water, in a porcelain dish or flask, and most of the acid in excess saturated with carbonate of soda, neutral tartrate of potash is then added in not too large quantity, and the precipitate so produced dissolved to a clear blue fluid by adding caustic potash or soda in excess; the vessel is then heated cautiously to about 150° Fahr., in the water-bath, and sufficient grape, milk, or starch sugar added to precipitate the copper present; the heating is continued until the precipitate is of a bright red colour and the upper liquid is brownish at the edges from the action of the alkali on the sugar; the heat must never exceed 190° Fahr. When the mixture has somewhat cleared, the upper fluid is poured through a moistened filter, and afterward the precipitate brought on the same, and washed with hot water till thoroughly clean; the precipitate which may adhere to the dish or flask is thoroughly washed, and the filter containing the bulk of the protoxide put with it, and an excess of solution of perchloride of iron (free from nitric acid or free chlorine) added, together with a little sulphuric acid, the whole is then warmed and stirred until the protochloride of copper is all dissolved. It is then filtered into a good-sized flask, the old and new filters being both well washed with hot water, to which, at first, a little free sulphuric acid should be added in order to be certain of dissolving all the oxide in the folds of the paper. The entire solution is then titrated with permanganate in the usual way, bichromate may also be used, but the end of the reaction is not so distinct as usual from the turbidity produced by the presence of copper.



**3. Fleitmann's Method, (results accurate.)**

The metallic solution, free from nitric acid, bismuth, or lead, is precipitated with zinc as in § 52, 1; the copper collected, washed, and dissolved in a mixture of perchloride of iron and hydrochloric acid; a little carbonate of soda may be added to expel the atmospheric air. The reaction is—



1 eq. of copper, therefore, produces 2 eq. protochloride of iron. When the copper is all dissolved, the solution is diluted and titrated with permanganate; 56 iron represent 31.7 copper.

If the original solution contains nitric acid, bismuth, or lead, the decomposition by zinc must take place in an ammoniacal solution, from which the precipitates of either of the above metals have been removed by filtration; the zinc must be finely divided and the mixture warmed; the copper is all precipitated when the colour of the solution has disappeared. It is washed first with hot water, then with weak hydrochloric or sulphuric acid and water, to remove the zinc; again with water, and then dissolved in the acid and perchloride of iron as before.

**4. Method of De Haen and E. O. Brown, (results accurate, in the absence of persalts of iron and other reducible substances.)**

The solution of the metal, if it contains nitric acid, is evaporated with sulphuric acid till the former is expelled, or the nitric acid is neutralized with carbonate of soda and acetic acid added, the sulphate solution must be neutral, or only faintly acid; excess of acetic acid is of no consequence.

The process is based on the fact that when iodide of potassium is mixed with a salt of copper in solution, diiodide of copper is precipitated as a dirty white powder, and iodine set free. If the latter is then titrated with decinormal hyposulphite and

starch liquor, the corresponding quantity of copper is found by the systematic factor.

Process: The solution, (containing not less than 1 Gm. Cu to each 100 CC,) free from iron, chlorine, or free nitric and hydrochloric acids, is brought into a beaker or flask, iodide of potassium in good quantity added, and the hyposulphite delivered from a burette till the brown colour has disappeared; starch liquor is then added, and decinormal iodine, to ascertain the excess of hyposulphite, or the titration may proceed direct by adding starch at first, and hyposulphite, till the blue colour is discharged.

Example: 10 CC of solution of sulphate of copper, containing 0.39356 Gm. = 0.1 Gm. copper was mixed with iodide of potassium in a beaker, and 19 CC of  $\frac{N}{10}$  hyposulphite added, then starch liquor, and 3.2 CC  $\frac{N}{10}$  iodine required to produce the blue colour = 15.8 CC hyposulphite; this multiplied by 0.006336 gave 0.1001 Gm. copper instead of 0.1 Gm.

In order to remove iron from copper solutions, previous to their analysis, it has been recommended to precipitate it with ammonia on the one hand, or to boil with acetate of soda on the other, and precipitating as basic acetate. In neither case can very satisfactory results be obtained, for with ammonia at least three precipitations are necessary to remove all the copper from the oxide of iron; boiling with acetate of soda does not always separate all the iron, and even if it should do so, the precipitate holds the copper tenaciously; the collection of fluid therefore, by these repeated precipitations and washings, is so considerable, that the process cannot be applied, except by evaporation, to a small bulk. The acetate of soda is far preferable to the ammonia, it must, however, be used in large quantity, and the precipitate washed with hot water containing acetate of soda. In certain cases, (i.e., where metals may be present which would interfere with the titration of the entire liquid by Parkes' process) it may be advisable to precipitate the iron by ammonia, slightly wash the precipitate, and then

push it through the funnel into a white capsule, and titrate with cyanide of potassium at once for the slight amount of copper present, adding the weight so found to that obtained in the filtrate by some other method.

5. Method of Parkes and C. Mohr, (results tolerably accurate, in the absence of manganese, nickel, cobalt, mercury, silver, and zinc.)

This well known and much used process for estimating copper depends upon the decoloration of an ammoniacal solution of copper by cyanide of potassium; the reaction (which is not absolutely uniform with variable quantities of ammonia) is such that a double cyanide of copper and ammonia is formed; cyanogen is also liberated, which reacts on the free ammonia, producing urea, oxalate of urea, cyanide and formiate of ammonium, (Liebig.) Owing to the influence exercised by variable quantities of ammonia, or its neutral salts, upon the decoloration of a copper solution by the cyanide, it is necessary that the solution analysed should contain pretty nearly the same proportion of ammonia as that upon which the cyanide has been originally titrated.

The experiments made by Fresenius shew this is absolutely necessary, and the undermentioned results, obtained by myself, point to the same conclusion.

1. 10 CC of solution of sulphate of copper, containing 0.10 Gm. Cu, with 1 CC of ammonia, spec. grav. .900, required 21.3 CC cyanide solution.

2. 50 CC of copper solution=0.50 Gm. Cu, and 5 CC ammonia required 106.5 CC cyanide.

These agree exactly.

3. 20 CC copper solution=0.20 Cu, with 6 CC ammonia required 43 CC cyanide, instead of 42.6.

4. 20 CC copper=0.20 Cu, with 20 CC ammonia, required 44 CC cyanide instead of 42.6.

The results with salts of ammonia were very similar.

It has generally been thought that where copper and iron occur together, it is necessary to separate the latter before using the cyanide. F. Field, however, has stated that this is not necessary, ("Chem. News," vol. i, p. 25,) and I can fully endorse his statement that the presence of the suspended oxide of iron is no hindrance to the estimation of the copper, in fact it is rather an advantage, as it acts as an indicator to the end of the process.

While the copper is in excess, the oxide possesses a purplish brown colour, but as this excess lessens, the colour becomes gradually lighter, until it is orange brown; if it be now allowed to settle, which it does very rapidly, the clear liquid above will be found nearly colourless. A little practice is of course necessary, to enable the operator to hit the exact point, and it is always well to make use of both indicators. The following experiment is given from among many others.

10 CC of copper solution = 0.10 Gm. Cu, were put into a small white porcelain dish, and 2 CC ammonia, .900 added, then the cyanide cautiously delivered from the burette, till the faintest violet tinge only was perceptible, the quantity so used was 21.3 CC; 10 CC of copper solution were then put into another dish, a little freshly precipitated peroxide of iron added, together with 2 CC ammonia. The cyanide was then delivered without looking at the burette, until the oxide had acquired the proper colour; the burette was found to stand at 21.3 CC, and the clear solution possessed the same faint tint as before.

Fleck ("Chem. Centralb.," page 22, 1860) has recommended the use of carbonate of ammonia instead of caustic, and the addition of two drops of solution of ferrocyanide of potassium, (1:20,) warming the solution to 60° C., (=145° Fahr.) the cyanide is delivered from the burette till the blue colour becomes faint, and when the reaction is complete, the reddish yellow colour of the ferrocyanide of copper suddenly appears,

but without any precipitate, if now another drop or two of cyanide is added, the liquid becomes colourless.

I have not been able to obtain very satisfactory results by this method, the ending not being sharp enough. I consider the oxide of iron by far the most sensitive reaction. It is best applied where carbonate of ammonia is used to remove other metals from the solution. In all cases where caustic ammonia is used, it is best to conduct the operation without heat, and in a small white porcelain dish.

**6. Pelouze's Process, (results tolerable accurate, in the absence of tin, nickel, cobalt, or silver.)**

This process is based on the fact that if an ammoniacal solution of copper is heated from  $140^{\circ}$  to  $180^{\circ}$  Fahr., and a solution of sulphide of sodium added, the whole of the copper is precipitated as oxysulphide,  $5\text{Cu S} + \text{Cu O}$ , leaving the liquid colourless. The loss of colour indicates, therefore, the end of the process, and this is its weak point; special practice, however, will enable the operator to hit the exact point closely.

**Preparation of Standard Solutions.**

It is first necessary to have a solution of pure copper, of known strength, which is best made by dissolving 39.356 Gm. of pure sulphate of copper in 1 litre, or 393.56 grn. in 10,000 grains of distilled water; each CC or dm. will respectively contain 0.01 Gm. or 0.1 grn. of pure metallic copper.

A measured quantity, say 50 CC, of standard solution of copper, is freely supersaturated with caustic ammonia, and heated till it begins to boil; the temperature will not be higher than  $180^{\circ}$ , in consequence of the presence of the ammonia; it is always well, however, to use a thermometer; the sulphide of sodium is delivered cautiously from a Mohr's burette, until the last traces of blue colour have disappeared from the clear

liquid above the precipitate. The experiment is repeated, and if the same result is obtained, the number of CC or dm. required to precipitate the amount of copper contained in 50 CC or dm., = 0.5 Gm. or 5 grn. respectively, is marked upon the sulphide of sodium bottle. As the strength of the solution gradually deteriorates, it must be titrated afresh every day or two. Special regard must be had to the temperature of the precipitation, otherwise the accuracy of the process is seriously interfered with.

## ZINC. Zn.—32.53.

## § 53.

Substance.	Formula.	Atomic Weight	Quantity to be weighed so that 1 CC or dm. of decinormal solution = 1 per cent. of substance.	$\frac{N}{10}$ Factor.
Zinc .....	Zn	32.53	0.3253 Gm., or 3.253 grn.	0.003253, or 0.03253
Oxide of Zinc ...	Zn O	40.53	0.4053 Gm., or 4.053 grn.	0.004053, or 0.04053
Carbonate of Zinc	Zn O, CO <sub>2</sub>	62.53	0.6253 Gm., or 6.253 grn.	0.006253, or 0.06253
Sulphide of Zinc	Zn S	48.53	0.4853 Gm., or 4.853 grn.	0.004853, or 0.04853

Metallic iron	×	0.5809 = zinc.
„	×	0.724 = oxide of zinc.
Double iron salt	×	0.3829 = zinc.
„ „	×	0.1039 = oxide of zinc.

1. Method of C. Mohr, (results accurate in the absence of manganese and the heavy metals in general.)

In the article on the analysis of ferridcyanide of potassium, by Lenssen's method, § 59, 1, it is shewn that greater exactness may be obtained through the use of an excess of zinc in

the mixture, so that the iodine liberated shall be the true measure of the substance.

In the present method the process may be considered to be reversed:—with an excess of ferridcyanide of potassium the liberated iodine shall express the true quantity of zinc sought.

If to a solution of zinc in acetic acid an excess of ferridcyanide of potassium is added, a reddish yellow precipitate of ferridecyanide of zinc occurs, having the composition,  $(\text{Cy}_6\text{Fe}_3)_3\text{Zn}$ .

If now to this mixture an excess of iodide of potassium be added, the decomposition occurs as follows. 2 at. ferridcyanide of zinc (expressing 6 at. zinc) react upon 2 at. iodide of potassium, producing 3 at. ferrocyanide of zinc, 2 at. acetate of potash, 1 at. ferrocyanic acid, and 2 at. free iodine; therefore, each equivalent of iodine, found by  $\frac{N}{10}$  hyposulphite, expresses 3 eq. of zinc, consequently, in any zinc analysis by this method, the number of CC or dm. of hyposulphite used must be multiplied by 3, and the product by the systematic factor.

The process is as follows:—

The metal and its compounds must exist in an acetic acid solution, which is best managed by dissolving the ores in *aqua regia*, evaporating to dissipate the excess of acid, neutralizing the remainder with carbonate of soda, then adding a strong solution of acetate of soda in excess, and boiling; then filter, and wash with boiling water containing a little acetate of soda; iron is removed by this means but not manganese, so that should the latter be present the process will not be applicable. In the presence of other metals the zinc must be separated as sulphide or oxide, and afterward brought into solution in acetic acid.

To the acetic acid solution so prepared a freshly-made solution of ferridecyanide of potassium is added in slight excess, (known by a drop of the mixture giving a blue colour with protosalts of iron), iodide of potassium in sufficient quantity is then added, together with starch liquor, and the titration with  $\frac{N}{10}$  hyposulphite performed as usual—1 eq. iodine=3 eq. zinc—the

greenish blue colour of the mixture entirely disappears, and gives place to the pure yellow of the red prussiate of potash, when in solution.

Fr. and C. Mohr and Fresenius have found the method very reliable. I have also found the same; it is not necessary, therefore, to give examples further than to say that in the case of pure salts of zinc 99·8 and 100·12 were obtained instead of 100.

## 2. Schwarz's Method, (results accurate.)

The principle of this method is based on the fact that when sulphide of zinc is mixed with perchloride of iron and hydrochloric acid—protochloride of iron, chloride of zinc, and free sulphur are produced: if the protochloride of iron is estimated with permanganate or bichromate of potash, the proportional quantity of zinc present is ascertained, 2 eq. Fe, represent 1 eq. Zn.

Ores of zinc are treated with hydrochloric, or in the case of blende, with that and nitric acid, dissolved, evaporated to dissipate excess of acid, and then precipitated with a mixture of carbonate and caustic ammonia, and digested warm till all the zinc precipitate is dissolved, the residue is washed with ammoniacal water and the filtrate and washings mixed. This ammoniacal solution, (which should contain all the zinc), is then warmed, and the zinc precipitated with a slight excess of sulphide of sodium or ammonium; when the precipitate has subsided the clear liquid is passed through a tolerably large and porous filter, the precipitate brought upon it, and well washed with warm water containing ammonia, till the washings no longer discolour an alkaline lead solution.

The filter with its contents is then pushed through the funnel into a good sized flask containing a sufficient quantity of perchloride of iron mixed with hydrochloric acid, immediately well stopped or corked, gently shaken, and put into a warm



place; after some time it should be again well shaken, and set aside quietly for about 10 minutes. After the action is all over the mixture should possess a yellow colour from the presence of undecomposed perchloride of iron, when the cork or stopper is lifted there should be no smell of sulphuretted hydrogen. The flask is then nearly filled with cold distilled water, some dilute sulphuric acid added, and titrated with permanganate or bichromate of potash as usual. The free sulphur and filter will have no reducing effect upon the permanganate if the solution is cool and very dilute.

Example: 1 Gm. pure oxide of zinc was dissolved in hydrochloric acid, supersaturated with ammonia, and precipitated with sulphide of ammonium, the precipitate well washed and digested with acid perchloride of iron, the whole was diluted to 500 CC in a stoppered flask, 100 CC titrated with permanganate of such strength that 120 CC=1 Gm. iron. 33.4 CC were required= $0.278$  Gm. iron, this multiplied by 5, as  $\frac{1}{5}$  only was taken, gave 1.390 Gm. iron, which multiplied by the factor for oxide of zinc 0.724 gave 1.0363 Gm. oxide of zinc, instead of 1 Gm.

Another 100 CC titrated with  $\frac{N}{10}$  bichromate, required 49.3 CC, which multiplied by the  $\frac{N}{10}$  factor, 0.004053 gave 0.1998129 Gm.  $\times 5 = 0.9990$  Gm.  $ZnO$ .

**3. Precipitation by Standard Sulphide of Sodium, with Alkaline Lead Solution as Indicator, applicable to most Zinc Ores and Products, (results accurate.)**

The ammoniacal solution of zinc is prepared just as previously described in Schwarz's method.

The standard sulphide of sodium is best made by saturating a portion of caustic soda solution with sulphuretted hydrogen, then adding sufficient soda solution to remove the smell of the free gas, and diluting the whole to a convenient strength for titrating.

The standard zinc solution is best made by dissolving 44.12 Gm. of pure sulphate of zinc to the litre, or 441.2 grn. to the 10,000 grns.; 1 CC or dm. will then contain 0.010 Gm. or 0.10 grn. of metallic zinc, and upon this solution, or one prepared from pure metallic zinc of the same strength, the sulphide of sodium must be titrated.

The alkaline lead solution used as indicator is made by heating acetate of lead, tartaric acid, and caustic soda solution in excess together until a clear solution is produced. It is preferable to mix the tartaric acid and soda solution first, so as to produce tartrate of soda, or if the latter salt is at hand it may be used instead of tartaric acid.

#### The Analytical Process.

50 CC of zinc solution = 0.5 Gm. Zn are put into a beaker, a mixture of solutions of ammonia and carbonate of ammonia, (3 of the former to about 1 of the latter,) added in sufficient quantity to redissolve the precipitate which first forms. A glass rod is then dipped into the lead solution and with it a few drops, placed at some distance from each other, on filtering paper, placed upon a slab or plate.

The solution of sulphide of sodium contained in an ordinary Mohr's burette is then suffered to flow into the zinc solution until, on bringing a drop from the mixture and placing it upon the filtering paper so that it may expand and run into the drop of lead solution, a black line occurs at the point of contact, the reaction is very delicate; at first it will be difficult, probably, to hit the exact point, but a second trial with 25 or 50 CC of zinc solution will enable the operator to be certain of the corresponding strength of the sulphide of sodium. As this latter is always undergoing a slight change, it is necessary to titrate for every day's use.

Direct titration with pure zinc solution gave 99.6 and 100.2, instead of 100.

C. Groll (*Zeitschrift für Analytische Chemie*, p. 21,) recommends the use of protochloride of nickel as indicator, instead of nitroprusside of sodium or lead. The drops are allowed to flow together on a porcelain plate; while the point of contact shows a blue or green colour the zinc is not all precipitated by the sulphide of sodium, therefore, the latter must be added until a grayish black colour appears at contact. I do not see any advantage over the lead paper in the process.

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#### COROLLARY.

##### Estimation of Alkaline Sulphides by Standard Zinc Solution.

§ 54. THIS method, which is simply a counterpart of the foregoing, is especially applicable for the technical determination of alkaline sulphides in impure alkalies, mother liquors, &c.

If the zinc solution be made by dissolving 3.253 Gm pure metallic zinc in hydrochloric acid, supersaturating with ammonia, and diluting to a litre, or 32.53 grn. to 10,000 grns. 1 CC or dm. will respectively indicate—

0.0016 Gm. or 0.016 grn.	sulphur
0.0039    „    or 0.039    „	sulphide of sodium
0.00551   „    or 0.0551   „    „	potassium
0.0034    „    or 0.034    „    „	ammonium

The zinc solution is added from a burette until a drop, brought in contact with the lead solution on filtering paper, no longer gives a black stain at the edges.

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**PEROXIDE OF MANGANESE.**

§ 55. 2 atoms protoxide of iron decompose 1 atom of peroxide of manganese, therefore  $56 \text{ Fe} = 43.57 \text{ Mn O}_2$ . 1 atom oxalic acid decomposes 1 atom peroxide manganese, therefore  $63 \text{ O} = 43.57 \text{ Mn O}_2$ .

**Factors.**

Metallic iron	×	0.178	= $\text{Mn O}_2$ .
Cryst. oxalic acid	×	0.6916	= ditto.
Double iron salt	×	0.111	= ditto.

1 CC or 1 dm. of decinormal permanganate, bichromate, or hyposulphite is equal to 0.004357 Gm. or 0.04357 grn. peroxide manganese.

The ores of manganese contain the metal in various states of oxidation, but as they are valued solely by the amount of available oxygen which they contain, it is invariably calculated as peroxide; therefore the above factors all apply to that substance.

Factors for the other oxides can be found readily if required.

All the oxides of manganese, with the exception of the first or protoxide, when boiled with hydrochloric acid yield chlorine equivalent to the oxygen contained in them above the first stage of oxidation. The chlorine so produced can be allowed to react upon a known weight of some protosalt of iron, and when the reaction is complete, the unchanged amount of iron salt is found by permanganate or bichromate.

Or, the reaction may take place with oxalic acid, resulting in the production of carbonic acid, which can be weighed as in Fresenius and Wills' method, or the amount of unchanged acid remaining after the action can be found by permanganate.

Or again, the chlorine so evolved may be led by a suitable arrangement into a solution of iodide of potassium, there setting free an equivalent quantity of iodine, which is found by the aid of hyposulphite of soda.

There are several other methods of analyzing the oxides of manganese, but as we have to do with the volumetric processes only, and with the best of them, the three here mentioned will be given in detail.

**1. Technical Examination of Manganese Ores, Pyrolusite, Braunite, Manganite, Psilomelane, &c.**

One of the most important things connected with the analysis of Manganese ores is the determination of moisture; and as most unpleasant disputes arise sometimes between analysts and those who buy and sell, simply because the sample examined by one analyst contained more or less moisture than one from the same bulk examined by another, it is always best to mention the amount of moisture found in the sample upon the certificate of analysis. Fresenius has found by a most careful series of experiments that the temperature at which all hygroscopic moisture is expelled, without disturbing that which is chemically combined, is 248° Fahr. (120° C), and this temperature is now used by most English and continental chemists. The drying apparatus devised by Fresenius consists of a round cast-iron air chamber, about ten inches in diameter and two inches deep, having six openings at the top, into which little brass pans, two-and-a-half inches diameter, are dropped, containing the very finely powdered ore; into one of the pans the bulb of a thermometer is placed, imbedded in iron filings, and the instrument kept upright by an iron rod and ring attached to the upper surface of the air chamber; the whole is supported by a tripod, and heated by a gas flame to the required temperature.

As only those who are continually analysing manganese ores would require a drying apparatus of this kind, a simpler contrivance is desirable for occasional use, and this is best managed

by a common iron ladle: it can be supported upon a retort ring, and heated by a gas or spirit lamp, using a tube thermometer for stirring the powder, and keeping it at a temperature of about  $245^{\circ}$  for about an hour, and lastly raising it to  $250^{\circ}$ , keeping it constantly stirred; then remove the heat, empty the powder into a porcelain crucible or dish, and let it cool somewhat under the exsiccator; before it is quite cold transfer to a small stoppered and accurately weighed bottle. The ore, when powdered and dried at this temperature, rapidly absorbs moisture on exposing it to the air, and consequently if a definite quantity has to be weighed it must be done quickly; therefore it is better to keep the powdered and dried sample in a small light stoppered bottle, the weight of which with its contents and stopper is accurately known; about 1 or 2 Gm. or any other quantity within a trifle can be emptied into the proper vessel for analysis, and the exact quantity found by re-weighing the bottle after the stopper is inserted.

A hardened steel or agate mortar must be used to reduce the mineral to the finest possible powder, so as to insure its complete and rapid decomposition by the hydrochloric acid.

**2. Direct Analysis by Distillation with Hydrochloric Acid, and  
Titrating with Hyposulphite of Soda.**

This is the quickest and most accurate method of finding the quantity of available oxygen present in any of the ores of Manganese or mixtures of them; it also possesses the recommendation that the quantity of chlorine which they liberate is directly expressed in the analysis itself; and further, gives an estimate of the quantity of hydrochloric acid required for the decomposition of any particular sample of ore, which is a matter of some moment to the manufacturer of bleaching powder.

The apparatus necessary for the operation is shown in Fig. 16, or instead of this, the arrangement devised by Fresenius or Bunsen may be used.

In order that the percentage of binoxide shall be directly expressed by the number of CC or dm. of  $\frac{N}{10}$  hyposulphite solution used, 0.436 Gm. or 4.36 grn. of the properly dried and powdered sample is weighed and put into the little flask; solution of iodide of potassium, in sufficient quantity to absorb all the iodine set free, is put into the large tube (if the solution containing  $\frac{N}{10}$  at. or 33.2 Gm. in the litre is used about 70 or 80 CC or dm. will in ordinary cases be sufficient); hydrochloric acid is then poured into the distilling flask, and the operation conducted as in § 45, 4.

Instead of using a definite weight, it is well to do as before proposed, namely, to pour about the quantity required out of the weighed sample bottle into the flask, and find the exact weight afterward. The titration proceeds as in § 45, 5.

### 3. Determination by Oxalic Acid.

The very finely powdered ore is brought in contact with a known volume of normal oxalic acid, sulphuric acid added, and the mixture warmed and well shaken to bring the materials in contact and liberate the carbonic acid; when the whole of the ore is decomposed, which may be known by the absence of brown or black sediment, the contents of the vessel are made up to a definite volume, say 300 CC and 100 CC of the dirty milky fluid, well acidified, diluted, and titrated for the excess of oxalic acid by permanganate; if, in consequence of the impurities of the ore, the mixture is brown or red-dish coloured, this would of course interfere with the reaction of the permanganate, and consequently the mixture in this case must be filtered; the 300 CC are therefore well shaken and poured upon a large and good filter; when about 100 CC have passed through, that quantity can be taken by the pipette and titrated as in the former case.

If the solution is not dilute and freely acid, it will be found that the permanganate produces a dirty brown colour instead of

its well known bright rose-red ; if the first few drops of permanganate produce the proper colour immediately they are added, the solution is sufficiently acid and dilute.

If 4.357 Gm. of the ore be weighed for analysis, the number of CC of normal oxalic acid will be the percentage of peroxide ; but as that is rather a large quantity, and takes some time to dissolve and decompose, half the quantity may be taken, when the percentage is obtained by doubling the CC of oxalic acid.

Example. The permanganate was titrated with normal oxalic acid and found that 10 CC = 2.5 CC normal oxalic, therefore, 1 CC = 0.25 CC normal oxalic. 2.178 Gm. of a fine sample of commercial manganese (Pyrolusite) was treated with 50 CC of normal oxalic acid, together with 5 CC of concentrated sulphuric acid until the decomposition was complete ; the resulting solution was milky, but contained nothing to hinder the colour of the permanganate, and, therefore, needed no filtration, it was diluted to 300 CC and 100 taken for titration, and required 6.2 CC permanganate ; a second 100 CC required 6.3, mean 6.25, which multiplied by 3 gave 18.75 CC, this multiplied by the factor 0.25 to convert it into oxalic acid, gave 4.68 CC normal oxalic, and this being deducted from the original 50 CC used, left 45.32 CC = 90.64% pure peroxide manganese.

This process possesses an advantage over the following, inasmuch as there is no fear of false results occurring from the presence of air ; the analysis may be broken off at any stage, and taken up at the operator's convenience.

#### 4. Determination by Iron.

The most satisfactory form of iron to be used in this process is the double salt of iron and ammonia, the equivalent number of which is 196, double this or 392 is required to decompose 1 eq. = 43.57 of peroxide of manganese, consequently, 1 Gm. pure peroxide requires 9 Gm. double salt ; or in order that the percentage shall be obtained without calculation 1.111 Gm. ore



may be weighed and digested in the presence of free hydrochloric acid, with 10 Gm. of double salt, the whole of which would be required supposing the sample was pure peroxide. The undecomposed iron salt remaining at the end of the reaction is estimated by permanganate or bichromate of potash, the quantity so found is deducted from the original 10 Gm., and if the remainder be multiplied by 10 the percentage is gained.

Instead of this plan, which necessitates exact weighing, any convenient quantity may be taken from the tared bottle, as before described, and digested with an excess of double salt, the weight of which is known; after the undecomposed quantity is found by permanganate or bichromate, the remainder is multiplied by the factor, 0.111, which gives the proportion of pure peroxide present, whence the percentage may be calculated.

Instead of the iron salt metallic iron may be used, but is much more troublesome and not so exact.

The decomposition of the ore may very conveniently be made in the flask apparatus, Fig. 18. The ore is first put into the decomposing flask, then the iron salt and water, so as to dissolve the salt to some extent before the hydrochloric acid is added, lest any free chlorine should escape; a little bicarbonate of soda may also be added to produce an atmosphere of carbonic acid. Strong hydrochloric acid should be used in considerable excess, and the flask heated by the spirit lamp till all the ore is decomposed; the solution is then cooled, diluted, and the whole or part titrated with permanganate (see § 43, 4) or bichromate. Instead of this apparatus, a single flask, with bent tube dipping under water, will be equally convenient.

Example: 1 Gm. of double iron salt, was titrated with permanganate solution, of which 21.4 CC were required.

A portion of the prepared ore was shaken out of the sample bottle, and found to weigh 1.24 Gm.; 10 Gm. of double salt, with a little water, was added, (where many manganese analyses are made, it is convenient to keep the required quantity weighed in homœopathic tubes well corked,) and hydrochloric acid poured

in: after the decomposition was complete 32.5 CC of permanganate were required to titrate the undecomposed iron salt, consequently

$$21.4 : 1 :: 32.5 : 1.51.$$

1.51 Gm., therefore, being deducted from 10 Gm., left 8.49 Gm., which multiplied by 0.111 gave 0.942 Gm. pure peroxide, whence the percentage is as follows—

$$1.24 : 0.942 \cdot 100 : x = 75.9 \%$$

1.111 Gm. of the same sample was accurately weighed and digested with 8 Gm. iron salt, with hydrochloric acid as before; after the decomposition, 8.8 CC of permanganate were required to peroxidise the undecomposed iron salt = 0.42 Gm., which deducted from the 8 Gm. originally used, left 7.58 Gm.; or placing the decimal point one place to the right, 75.8 % pure peroxide manganese.

In the last example, 8 Gm. of iron salt were used, because from the former experiment I knew the percentage of the ore, and therefore did not need to exceed the required quantity to any extent. It is always advisable to do this, where possible, as there is then less chance of error from the presence of air; as most samples do not exceed 80 per cent., 8 Gm. is sufficient.

The advantages possessed by this process over the former are that stronger hydrochloric acid may be used, and less time is occupied in the process.

In the case of using decinormal bichromate of potash for the titration, the following plan is convenient: 100 CC or dm.  $\frac{N}{10}$  bichromate = 4.032 Gm. or 40.32 grn. double iron salt; therefore, if 0.436 Gm. or 4.36 grn. of the sample of ore is boiled with 4.032 Gm. or 40.32 grn. of the double salt and acid, the number of CC or dm. of bichromate required will be the percentage

Example: 4.36 grn. of the same sample as examined before, was boiled with 40.32 grn. double salt, and afterward required 24 dm. of  $\frac{N}{10}$  bichromate, which deducted from 100 leaves 76 % peroxide, agreeing very closely with the previous examinations.

## PROTOXIDE OF MANGANESE.

Mn O=35.57.

Factor for  $\frac{M}{V}$  permanganate, 0.003557 Gm., or 0.03557 grn.Ferrocyanide of potassium.  $\times$  0.0842 = Mn O.Double iron salt  $\times$  0.0911 = „

§ 56. If protoxide or a protosalt of manganese is boiled with an alkaline solution of red prussiate of potash, the latter becomes converted into ferrocyanide, while the manganese precipitates as hydrated peroxide. Lenssen found, however, that the composition of the precipitate was not uniform; that is to say, its state of oxidation, unless at least 1 eq. of peroxide of iron was added with every eq. of manganese. The precipitate, under these circumstances, possesses a constant composition. The amount of manganese present is indirectly found by titrating the resulting ferrocyanide of potassium with permanganate, 2 eq. of which=1 eq. Mn O.

The results are very satisfactory with certain precautions suggested by Fresenius, namely:—

1. That the solution of caustic potash or soda used must be free from organic matter; if pure solid alkalies are used, they should be fused in a silver crucible before being added.
2. That the boiling must not be continued too long, for if pure potash and ferridcyanide are boiled for some considerable time, traces of ferrocyanide are produced.
3. The precipitate must be exceedingly well washed; and being rather voluminous this occupies some time.

## The Analytical Process.

The acid solution of protoxide of manganese is mixed with a solution of perchloride of iron, in such proportion that not less than 1 eq.  $Fe_2 O_3$  is present with every eq. of Mn O. The

mixture is then added, little by little, to a boiling alkaline solution of ferridcyanide of potassium; after a few minutes boiling, the precipitate becomes granular, and shrinks somewhat. The flask is then put aside till *quite* cold, (the hot solution would be affected by the reducing action of the filter,) then filtered and thoroughly washed; the filtrate, or a portion of it, titrated, after acidifying with sulphuric acid and warming, with permanganate, as in § 58, 4.

A shorter but somewhat less exact method is to dilute the mixture after boiling, to a definite volume, say 300 CC; allow to settle thoroughly; then take out 100 CC or so for titration. The bulky precipitate interferes, to a small extent, with the accurate measurement of the liquid; and this difficulty is increased when a great excess of oxide of iron is present. A mean of five determinations made by Fresenius on this plan, using only a slight excess of iron, gave 99.12 instead of 100; therefore quite satisfactory for cases where the greatest accuracy is not required.

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TIN. Sn—59.

Metallic iron	×	1.0536	= Tin.
Double iron salt	×	0.1505	= „
Factor for $\frac{N}{10}$ iodine or permanganate of potash solution		0.0059	

§ 57. THE method originally devised by Streng, for the direct estimation of tin by bichromate of potash, or other oxidising agents in acid solution, has been found most unsatisfactory, from the fact that variable quantities of water or acid seriously interfere with the accuracy of the results. The cause is not fully understood, but that it is owing partly to the

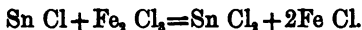
oxygen mechanically contained in the water reacting on the very sensitive protochloride of tin, there can be very little doubt, as the variations are considerably lessened by the use of water recently boiled and cooled in closed vessels. These difficulties are set aside by the processes of Lenssen, Löwenthal, Stromeyer, and others, now to be described, and which I have myself found satisfactory.

**1. Direct Titration by Iodine in Alkaline Solution, (Lenssen.)**

Metallic tin or its protosalt is dissolved in hydrochloric acid, if not already in solution, a tolerable quantity of the double tartrate of soda and potash added, together with bicarbonate of soda in excess. If enough tartrate is present, the solution will be clear; starch liquor is then added, and the mixture titrated with  $\frac{N}{10}$  iodine, till the blue colour is permanent; metallic tin is best dissolved in hydrochloric acid by placing a platinum crucible or cover in contact with it so as to form a galvanic circuit.

**2. Indirect Titration by Perchloride of Iron and Permanganate of Potash, (Löwenthal, Stromeyer, &c.)**

This method owes its value to the fact that when protochloride of tin is brought into contact with perchloride of iron or copper, it acts as a reducing agent, in the most exact manner, upon these compounds, perchloride of tin being formed, together with a proportionate quantity of protochloride of iron or copper, as the case may be; if either of the latter be then titrated with permanganate, the original quantity of tin may be found, the reaction being, in the case of iron,—



Iron=59 tin. If decinormal permanganate, or the factor

necessary to convert it to that strength, be used, the calculation by means of iron is not necessary.

The solution of protochloride, or other protosalt of tin in hydrochloric acid, is mixed with pure perchloride of iron, diluted with distilled water, and titrated with permanganate as usual; to obtain the most exact results, it is necessary to make an experiment with the same permanganate upon a like quantity of water, to which perchloride of iron is added; the quantity required to produce the same rose colour is deducted from the total permanganate, and the remainder calculated as tin.

Perchloride, peroxide, and other persalts of tin, also tin compounds containing iron, are dissolved in water, hydrochloric acid added, and a plate of clean zinc introduced for ten or twelve hours, the tin so precipitated is carefully collected and washed, then dissolved in hydrochloric acid, and titrated as above; or the finely divided metal may at once be mixed with an excess of perchloride of iron, a little hydrochloric acid added, and when solution is complete, titrated with permanganate; the reaction in this latter case is expressed as follows:

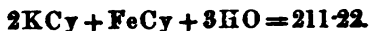


therefore 4 eq. iron (=112) occurring in the form of protochloride represent 1 eq. (=59) tin.

Tin may also be precipitated from slightly acid peroxide solution, as sulphide, by sulphuretted hydrogen gas or water, the sulphide well washed, and mixed with perchloride of iron; the mixture gently warmed, and the sulphur filtered off; the filtrate then titrated with permanganate as above, 4 eq. iron = 1 eq. tin.

## YELLOW AND RED PRUSSIATES OF POTASH.

Ferrocyanide of Potassium,



Metallic iron       $\times$  7.541 = crystallized ferrocyanide of potassium.

Double iron salt    $\times$  1.077 = Ditto.

## 1. De Haen's Method.

§ 58. This substance may be estimated by permanganate of potash, which acts by converting it into red prussiate. The process is easy of application, and the results accurate. De Haen recommends that a standard solution of pure ferrocyanide should be used as the basis upon which to work, and this is advisable; it can, however, be dispensed with, if the operator chooses to calculate the strength of his permanganate upon iron or its compounds. If the permanganate is decinormal, there is of course very little need for calculation, (2 eq. = 422.44 must be used as the systematic number, and therefore 1 CC of  $\frac{N}{10}$  permanganate is equal to 0.042244 Gm. of yellow prussiate.) The standard solution of pure ferrocyanide contains 20 Gm. in the litre, or 200 grn. in the 10,000 gra.; each CC will contain 0.020 Gm., each dm. 0.20 grn.

## The Analytical Process.

10 CC of the standard prussiate solution are put into a white porcelain dish, or beaker standing on white paper, and 250 CC or so of water added; it is then acidified pretty strongly with sulphuric acid, and the permanganate delivered from the burette until the pure yellow colour disappears, and gives place to a beautiful uranium yellow colour: it is then cautiously added until the faintest pink tinge occurs. De Haen, Fresenius,

and Mohr all agree in stating that the end of the reaction is hindered by turbidity; this I have not found to be the case, but have invariably found that when the solution of ferrocyanide is very dilute, say  $\frac{1}{2}$  Gm. to 10 or 12 oz. water freely acidified, and the operation performed in a clean white evaporating basin, that the mixture remains clear, and the end is very exactly shewn; a drop or two in excess of permanganate being sufficient to give the necessary pinkish tinge. I attribute the different experience obtained by us to the fact that I invariably use pure permanganate of potash for titration, and sulphuric instead of hydrochloric acid.

## 2. Titration with Bichromate of Potash.

In the "Chemical News," vol. iii, No. 74, Professor Davy, of Dublin, describes a method for the valuation of bleaching powder, by the aid of a standard solution of ferrocyanide of potassium, which consists in adding an excess of the ferrocyanide to a given weight of bleaching powder, and afterward ascertaining the amount of ferrocyanide unconverted into ferridcyanide by standard bichromate of potash. A solution of perchloride of iron is used as the indicator for the residual process with bichromate; so long as a greenish blue colour is produced by bringing the rod with which the mixture is stirred in contact with a drop of the iron solution, the ferrocyanide is in excess, but when this gives place to a yellowish brown colour, the bichromate is in excess.

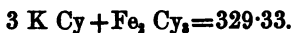
I regret that after spending considerable time over this method, for the purpose of verifying Davy's statements, I have been compelled to give it up as useless; it would have been a great boon if a stable and commercially pure salt, like the ferrocyanide, could be used with exactness in volumetric analysis, but so far as its reaction with bichromate of potash is concerned, it does not fulfil this condition. If two solutions of decinormal strength are made, namely, bichromate of potash,



$\frac{3}{4}$  at. = 4.919 Gm. in litre, and ferrocyanide of potassium,  $\frac{1}{2}$  at. = 42.244 Gm. in litre; they should be of the same chemical power, and drop for drop combine with each other to produce the reaction above mentioned. This, however, is not the case, for if 10 CC of the ferrocyanide solution be put into a beaker, acidified with hydrochloric or sulphuric acid, and the bichromate added from the burette, until a drop of the mixture produces a yellowish brown colour with perchloride of iron, it will be found that the point is reached when 9.5 CC of bichromate have been added. On finding this to be the case, I prepared absolutely pure salts and fresh solutions, with the same result. I then tried a solution of acetate of uranium as indicator, with precisely the same results. The ferrocyanide solution was then titrated with  $\frac{N}{10}$  permanganate, (previously titrated both on pure iron and the double salt,) and equal volumes exactly were required, shewing that the apparent discrepancy did not arise from any error in calculating the atomic proportions of the two salts; a vast number of experiments were made, in every way likely to throw light upon the matter, but with no satisfactory conclusion, except that the method must be rejected as untrustworthy, even for technical purposes; sometimes the characteristic reaction with the indicator occurred at 9.2 CC of bichromate to 9.3 and 9.4, but never below 9.5 CC.

The loss, therefore, when calculating an analysis by this method would never be less than 5 per cent., and might be more. Davy makes the remark, that in testing this process for the estimation of bleaching powder, side by side with those of Gay Lussac and Otto, he invariably found that more chlorine was shown to be present than in the two latter processes, and which he attributes to an unavoidable loss of that substance in their methods; but I think there can be no doubt that he is wrong in this supposition, for as above shown there is in his process a constant loss of ferrocyanide, which in calculating the analysis would result in a gain of chlorine; had it not been a residual method, the error would have been large enough to detect itself.

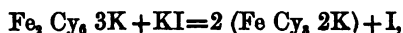
## FERRIDCYANIDE OF POTASSIUM.



Metallic iron	$\times 5.88$	= Ferridcyanide of potass.
Double iron salt	$\times 1.68$	= " "
$\frac{N}{10}$ Hyposulphite of soda	$\times 0.032933$	= " "

## 1. Lenssen's Method.

§ 59. This salt can be estimated either by reduction to ferrocyanide and titration with permanganate or bichromate of potash as above, or by Lenssen's method, which is based upon the fact, that when iodide and ferridcyanide of potassium are mixed with tolerably concentrated hydrochloric acid, iodine is set free.



the quantity of which can be estimated by  $\frac{N}{10}$  hyposulphite and starch liquor; this method does not, however, give the most satisfactory results, owing to the variation produced by working with dilute or concentrated solutions. C. Mohr's modification (see Zinc, § 53,) is, however, more reliable, and is as follows. The ferridcyanide is dissolved in a convenient quantity of water, iodide of potassium in crystals added, together with hydrochloric acid in tolerable quantity, then a solution of pure sulphate of zinc in excess; after standing a few minutes to allow the decomposition to perfect itself, the excess of acid is neutralized by carbonate of soda, so that the latter slightly predominates.

At this stage all the ferridcyanide of zinc first formed is converted into the ferrocyanide of that metal, and an equivalent quantity of iodine set free, which can at once be titrated with  $\frac{N}{10}$  hyposulphite and starch, and with very great exactness. 1 CC  $\frac{N}{10}$  hyposulphite = 0.032933 Gm. ferridcyanide of potassium.

The mean of five determinations made by Mohr gave 100.21 instead of 100.

## 2. Reduction of Ferrid to Ferrocyanides.

This process is of course necessary when the determination by permanganate of potash has to be made, and is best effected by boiling the weighed ferridcyanide with an excess of potash or soda, and adding small quantities of concentrated solution of protosulphate of iron until the precipitate which occurs possesses a blackish colour (signifying that the magnetic oxide is formed); the solution is then diluted to a convenient quantity, say 300 CC, well mixed and filtered through a dry filter; 50 or 100 CC can then be taken, sulphuric acid added, and titrated with permanganate as before described.

Other soluble ferro or ferridcyanides can be examined in the same way as the potassium salts, and if insoluble they may generally be converted into the latter by boiling with strong caustic potash.

## LIME. Ca O = 28.

1 CC or 1 dm. $\frac{N}{10}$ permanganate	= 0.0028 Gm. or 0.028 grn	Ca O
" " "	= 0.0050 Gm. or 0.050 grn.	Ca O, CO <sub>2</sub>
" " "	= 0.0086 Gm. or 0.086 grn.	Ca O, SO <sub>3</sub> + 2 HO,
" normal oxalic acid	= 0.0280 Gm. or 0.280 grn.	Ca O

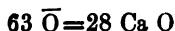
Cryst. oxalic acid  $\times 0.444$  = Ca O

Double iron salt  $\times 0.07143$  = "

§ 60. THE estimation of lime alkalimetrically has already been given, but that method is of limited application, unless oxalate of lime, in which form lime is generally separated from

other bases, be converted into carbonate or caustic lime by ignition, and thus determined with normal nitric acid and alkali. This and the following method by Hempel are as exact in their results as the determination of lime by weight; and where a series of estimations have to be made, the plan is very convenient—

1. The lime is precipitated by oxalate of ammonia from an ammoniacal or acetic acid solution, the precipitate well washed, then together with the filter pushed through the funnel into a large flask, acidified and diluted freely; then titrated with permanganate, as described in § 43, 3.



2. Is applicable in certain cases only, but saves time when it can be applied. To the lime solution (which must contain no substance capable of decomposing permanganate) a measured excess of normal oxalic acid is added; the precipitated oxalate of lime allowed to settle in a 300 CC flask, and 100 CC of the clear liquid acidified and titrated for the excess of oxalic acid; the quantity so found is multiplied by 3, deducted from that originally added, and the remainder multiplied by the factor for normal oxalic acid.

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LEAD, Pb.—103.50.

Factor for decinormal

permanganate ..... 0.01035 Gm. or 0.1035 grn.

Factor for normal oxa-

lic acid ..... 0.1035 Gm. or 1.035 grn.

Metallic iron            × 1.848 = Lead

Double iron salt        × 0.264 = „

Crystallized oxalic acid × 1.643 = „

§ 61. The estimation of lead is in most cases more securely effected by weight than by measure; there are, however, instances in which the latter process may be used with advantage, and consequently the following methods are given:—

**1. Hempel's Method (modified.)**

The lead solution, which must contain no other body precipitable by oxalic acid, is put into a 300 CC or dm. flask, and a measured quantity of normal oxalic acid added in excess, ammonia is then added to slight predominance, the flask filled to the mark with water, shaken, and put aside to settle; 100 CC or dm. of the clear liquid may then be taken, acidified with sulphuric acid, and titrated for the excess of oxalic acid with permanganate; the amount so found multiplied by 3 and deducted from that originally added will give the quantity combined with the lead.

Where the nature of the filtrate is such that permanganate cannot be used for titration, the precipitate must be collected, well washed, dissolved in dilute nitric acid, sulphuric acid added, and titrated with permanganate.

In neither case are the results absolutely accurate, owing to the slight solubility of the precipitate, but with careful manipulation the error need not exceed 1 per cent.

**2. Schwarz's Method, (results accurate.)**

The lead is precipitated as chromate, well washed, and digested with a weighed excess of double iron salt, and hydrochloric acid—the result is perchloride of iron, chloride of chromium, and chloride of lead, together with undecomposed iron salt. The quantity of the latter is found after filtering off the chloride of lead, by permanganate, and deducted from the original weight; the remainder multiplied by the factor 0.264, will give the weight of lead.

### 3. Mohr's Alkalimetric Method, (results tolerably accurate.)

The lead is precipitated as carbonate by means of a slight excess of carbonate of ammonia, together with free ammonia, the precipitate well washed, and dissolved in a measured excess of normal nitric acid, neutral solution of sulphate of soda is then added to precipitate the lead as sulphate; without filtering, the excess of nitric acid is then estimated by normal alkali, each CC or dm. combined being equal to 0.1035 Gm. or 1.035 grn. lead.

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### MERCURY. Hg.=100.

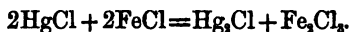
Factor for $\frac{N}{10}$ solutions of permanganate, iodine,			
or salt.....	0.0200 Gm. or 0.200 grn. Hg		
	0.0208	„	0.208 „ HgO
	0.0271	„	0.2710 „ HgCl
Double iron salt	×	0.5104	= Hg
„ „	×	0.6914	= HgCl

### 1. Precipitation as Protochloride by Decinormal Salt Solution, and estimation of the excess of Salt by Decinormal Silver and Chromate of Potash, (results accurate.)

§ 62. THE solution to be titrated must not be warmed, and contain the metal only in the form of protoxide. The salt solution is added in slight excess, the precipitate washed with the least possible quantity of water to ensure the removal of all the salt, to the filtrate a few drops of chromate solution are added, then pure carbonate of soda till the liquid is of clear yellow colour,  $\frac{N}{10}$  silver is then delivered in till the red colour occurs. The quantity of salt so found is deducted from that originally used, and the difference calculated in the usual way. § 74.

2. *Mohr's Method.*

This process is based on the fact that when perchloride of mercury (sublimate) is brought in contact with an alkaline solution of protoxide of iron in excess, the latter is converted into peroxide while the mercury is reduced to protochloride, (calomel,) the excess of protoxide of iron is then found by permanganate or bichromate of potash—



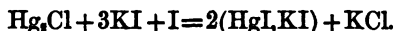
It is therefore advisable in all cases to convert the mercury to be estimated into the form of sublimate, secured by evaporating it to dryness with nitro-hydrochloric acid, this must take place, however, below boiling heat, as vapours of chloride escape with steam at 212° Fahr. (Fresenius.)

Nitric acid or free chlorine must be altogether absent during the decomposition with the iron protosalt, otherwise the residual titration will be inexact, and the quantity of the iron salt must be more than sufficient to absorb half the chlorine in the sublimate.

Example: 1 Gm. pure sublimate was dissolved in warm water and 3 Gm. double iron salt added, then solution of caustic soda till freely alkaline. The mixture became muddy and dark in colour and was well shaken for a few minutes, then chloride of sodium and sulphuric acid added, continuing the shaking till the colour disappeared and the precipitate of oxide of iron dissolved, leaving the calomel white: it was then diluted to 300 CC, filtered through a dry filter, and 100 CC titrated with  $\frac{N}{10}$  permanganate, of which 13.2 CC were required—multiplied by 3=39.6, which deducted from 76.5 CC, (the quantity required for 3 Gm. double iron salt,) left 36.9 CC=1.446 Gm. undecomposed iron salt, which multiplied by the factor 0.6914, gave 0.999 Gm. sublimate, instead of 1 Gm., or the 36.9 CC may be multiplied by the  $\frac{N}{10}$  factor for chloride of mercury, which will give the same figures exactly.

## 3. Hempel's Method, (results accurate.)

If the mercury exists as a protosalt it is precipitated by chloride of sodium, the precipitate well washed, and together with its filter pushed through the funnel into a stoppered flask, a sufficient quantity of iodide of potassium added, together with  $\frac{N}{10}$  iodine solution, (to 1 Gm. calomel about 2.5 Gm. of iodide, and 100 CC  $\frac{N}{10}$  iodine,) the flask closed, and shaken till the precipitate has dissolved—



The brown solution is then titrated with  $\frac{N}{10}$  hyposulphite till colourless, then diluted to a definite volume, and a measured portion titrated with  $\frac{N}{10}$  iodine and starch for the excess of hyposulphite—1 CC  $\frac{N}{10}$  iodine = 0.02 Gm. Hg.

Where the mercurial solution contains nitric acid or the metal exists as peroxide, it may be converted into protochloride by the reducing action of protosulphate of iron, as in Mohr's method. The solution must contain hydrochloric acid or common salt in sufficient quantity to transform all the mercury into calomel. At least three times the weight of mercury present of protosulphate of iron in solution is to be added, then caustic soda in excess, the muddy liquid well shaken for a few minutes, then dilute sulphuric acid added in excess, and the mixture stirred till the dark coloured precipitate has become perfectly white. The calomel so obtained is collected on a filter, well washed, and titrated with  $\frac{N}{10}$  iodine and hyposulphite as above.

4. Direct Titration with Hyposulphite of Soda, (Scherer,) results accurate in the absence of other metals precipitable by hyposulphite.)

The solution of hyposulphite is in all cases made by dissolving  $\frac{1}{10}$  eq. = 12.4 Gm. of the salt in 1 litre of water, or by mixing equal volumes of  $\frac{N}{10}$  hyposulphite and distilled water.



**c Determination as Protoxide.**

The solution containing the metal only as a protosalt is diluted, gently heated, and the hyposulphite delivered in from the burette at intervals, meanwhile well shaking until the last drop produces no brown colour. The sulphide settles freely and allows the end of the reaction to be easily seen. 1 CC of hyposulphite solution is equal to 0.020 Hg, or 0.0208 HgO.

**d As Nitrate of Peroxide.**

The solution is considerably diluted, put into a stoppered flask, nitric acid added, and the hyposulphite cautiously delivered from the burette, vigorously shaken meanwhile until the last drop produces no further yellow precipitate. ( $2\text{HgS} + \text{HgO}, \text{NO}_3$ .) Scherer recommends that when the greater part of the metal is precipitated, the mixture should be diluted to a definite volume, the precipitate allowed to settle, and a measured quantity of the clear liquid taken for the completion of the process, the analysis may then be checked by a second titration of the clear liquid, if needful. 1 CC hyposulphite is equal to 0.015 Hg, or 0.0162 HgO.

With perchloride of mercury (sublimite) the end of the process is not so easily seen; the course of procedure is as follows:—The very dilute solution is acidified with hydrochloric acid, heated nearly to boiling, and the hyposulphite cautiously added so long as a white precipitate is seen to form; any great excess of the precipitant produces a dirty looking colour. Filtration is necessary to distinguish the exact ending of the reaction, for which purpose Dr. Beale's filter, Fig. 15, is useful.

Liebig's method is the reverse of that used for determining chlorides in urine, § 80, 2, 3, phosphate of soda being used in the estimation of mercury as indicator, instead of the urea occurring naturally in the urine. The method is capable of very slight application.

## GOLD. Au—196·67.

1 dm. normal oxalic acid=0·6556 Gm. Gold.

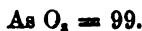
§ 63. THE technical assay of gold for coining purposes is invariably performed by cupellation. Terechloride of gold is, however, largely used in photography, and, therefore, it may be necessary sometimes to ascertain the strength of a solution of the chloride or its value as it occurs in commerce.

If to a solution of gold in the form of chloride, (free from nitric acid,) an excess of oxalic acid be added, in the course of from 18 to 24 hours all the gold will be precipitated in the metallic form, while the corresponding quantity of oxalic acid has been dissipated in the form of carbonic acid; if, therefore, the quantity of oxalic acid originally added be known, and the excess, after complete precipitation of the gold, be found by permanganate of potash, the measure of gold will be obtained.

Example: A 15 grain bottle of the chloride of gold of commerce was dissolved in water, and the solution made up to 300 decems.\* 20 dm. of normal oxalic acid were then added, and the flask set aside for twenty-four hours in a warm place, at the end of that time the gold had settled, and the supernatant liquid was clear and colourless. 100 dm. were taken out with a pipette, and titrated with  $\frac{N}{10}$  permanganate, of which 25 dm. were required; this multiplied by 3 gives 75 dm.=7·5 dm. normal oxalic acid, which deducted from the 20 dm. originally added, left 12·5 dm.; this multiplied by  $\frac{1}{3}$ rd the equivalent of gold (1 eq. chloride of gold decomposing 3 eq. oxalic acid)=0·6556 gave 8·195 grn. metallic gold, or multiplied by 101 (=1/3 eq. chl. gold) gave 12·625 grn.; either way the result was 84 per cent. of chloride of gold instead of 100.

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## ARSENIOUS ACID.

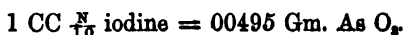


## 1. Oxidation by Iodine, (Mohr, results accurate.)

§ 64. THE principle upon which the determination of this substance by iodine is based is explained in § 46.

It therefore only remains to say, that in the estimation of arsenious acid or its compounds by the method there described, it is advisable to use bicarbonate of soda for rendering the solution alkaline in preference to the neutral carbonate, as there is less chance of the iodine being affected by the bicarbonate than by the neutral salt.

To a neutral or watery solution, therefore, it is best to add about 20 or 25 CC of saturated solution of pure bicarbonate to every 0.1 Gm. or so of  $\text{As O}_3$ , and then titrate with  $\frac{N}{10}$  iodine and starch. When the solution is acid, the excess may be removed by neutral carbonate of soda, then the necessary quantity of bicarbonate added, and the titration completed as before.



## 2. Indirect Estimation by Distilling with Chromic and Hydrochloric Acids, (Bunsen.)

The principle of this very exact method depends upon the two facts, that when bichromate of potash is boiled with concentrated hydrochloric acid, chlorine is liberated in the proportion of 3 eq. to 2 eq. chromic acid. See § 65, 2.

If, however, arsenious acid is present, but not in excess, the chlorine evolved is not in the proportion mentioned above, but so much less as is necessary to convert the arsenious into arsenic acid.

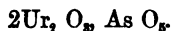


Therefore every 2 eq. of chlorine, short of the quantity yielded when bichromate and hydrochloric acid are distilled alone, represent 1 eq. arsenious acid. The operation is conducted in the apparatus Fig. 16, and the titration as in § 45, 4, 5.

**By Precipitation as Arseniate of Uranium, (Bödeker, results accurate.)**

The arsenic must exist in the state of arsenic acid ( $\text{As O}_5$ ) and the process is in all respects the same as for the estimation of phosphoric acid, devised by Neubauer, Pincus, and myself, § 78, 1. The strength of the uranium solution may be ascertained and fixed by pure arseniate of soda or potash, or by means of a weighed quantity of pure arsenious acid converted in arsenic acid by boiling with strong nitric acid. For the details of the process see § 78, 1.

The precipitate of arseniate of uranium possesses the composition—



**CHROMIUM. Cr = 52.04.**

**Factors.**

Metallic iron	×	0.3123	= Chromium
"	×	0.598	= Chromic acid
"	×	0.8784	= Bichromate of potash
"	×	1.926	= Chromate of lead
Double iron salt	×	0.0446	= Chromium
"	×	0.0854	= Chromic acid
"	×	0.1255	= Bichromate of potash
"	×	0.275	= Chromate of lead

§ 65. 1. THE estimation of chromates is very simply and successfully performed by the aid of protoxide of iron, being the converse of the process devised by Penny for the estimation of iron. See § 44.

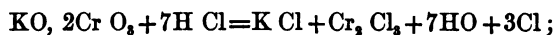
The best plan of procedure is as follows. A very small beaker or other convenient vessel is partly or wholly filled, as may be requisite, with perfectly dry and granular double sulphate of iron and ammonia; the exact weight then taken and noted. The chromium compound is brought into solution, not too dilute, acidified with sulphuric acid and small quantities of the iron salt, added from time to time with a dry spoon, taking care that none is spilled, until the mixture becomes green, and the iron is in excess, best known by a small drop being brought in contact with a drop of red prussiate of potash on a white plate; if a blue colour appears at the point of contact, the iron is in excess. It is necessary to estimate this excess, which is most conveniently done by  $\frac{N}{10}$  bichromate being added until the blue colour produced by contact with the red prussiate gives place to a yellow brown. The vessel containing the iron salt is again weighed, the loss noted; the quantity of the salt represented by the  $\frac{N}{10}$  bichromate deducted from it, and the remainder multiplied by the factor required by the substance sought.

Example: 0.5 Gm. pure bichromate of potash was taken for analysis, and to its acid solution 4.15 Gm. double iron salt added. 3.3 CC of  $\frac{N}{10}$  bichromate were required to oxidise the excess of iron salt; it was found that 0.7 Gm. of the salt = 17.85 bichromate solution, consequently 3.3 CC of the latter were equal to 0.12985 Gm. iron salt; this deducted from the quantity originally used left 4.02015 Gm., which multiplied by the factor 0.1255 gave 0.504 Gm. instead of 0.5 Gm.

In the case of chromate of lead being estimated in this way, it is best to mix both the chromate and the iron salt together in a mortar, rubbing them to powder, adding hydrochloric acid, stirring well together, then diluting with water and titrating as before.

**2. Estimation of Chromates by Distillation with Hydrochloric Acid,  
(Bunsen, results very accurate.)**

When chromates are boiled with an excess of hydrochloric acid in Fresenius', Bunsen's, or Mohr's distilling apparatus, Fig. 16, every 2 eq. of chromic acid liberate 3 eq. chlorine. For instance, with bichromate of potash the reaction may be expressed as follows—



if the liberated chlorine is conducted into a solution of iodide of potassium, 3 eq. of iodine are set free, and can be estimated by  $\frac{\text{N}}{10}$  hyposulphite, as in § 45. 3 eq. of iodine so obtained = 381, represent 2 eq. chromic acid = 100.40. The same decomposition takes place by mere digestion, as described in § 45, 4.

**ANTIMONY. Sb — 122.**

**1. Conversion of Oxide of Antimony in Alkaline Solution into  
Antimonie Acid by Iodine, (Mohr, results accurate.)**

§ 66. THE oxide of the metal, or any of its compounds, is brought into solution as tartrate by tartaric acid and water; the excess of acid neutralized by neutral carbonate of soda, then a cold saturated solution of bicarbonate of soda added in the proportion of 20 CC to about 0.1 Gm. Sb O<sub>3</sub>; to the clear solution starch liquor and  $\frac{\text{N}}{10}$  iodine are added until the blue colour appears; the colour disappears after a little time, therefore the first appearance of a permanent blue is accepted as the true measure of iodine required.

$$1 \text{ CC } \frac{\text{N}}{10} \text{ iodine} = 0.0061 \text{ Gm Sb.}$$

**2. Distillation of Ter or Pentasulphide of Antimony with Hydrochloric Acid, and Titration of the evolved Sulphuretted Hydrogen, (Schneider, results accurate.)**

When either of the sulphides of antimony are heated with hydrochloric acid in Bunsen's, Fresenius', or Mohr's distilling apparatus, Fig. 16, for every 1 eq. of antimony present as sulphide 3 eq. of sulphuretted hydrogen are liberated. If therefore the latter be estimated, the quantity of antimony is ascertained. The process is best conducted as follows:—

The antimony to be determined is brought into the form of ter or pentasulphide, (if precipitated from a hydrochloric solution, tartaric acid must be previously added, to prevent the precipitate being contaminated with chloride,) which together with the filter containing it, is put into the distilling flask with a tolerable quantity of hydrochloric acid not too concentrated. The condensing tube, Fig. 16, contains a mixture of caustic soda or potash, with a definite quantity of  $\frac{N}{10}$  arsenious acid solution, § 46, 1, in sufficient excess to absorb all the sulphuretted hydrogen evolved. The flask is then heated to boiling, and the operation continued till all evolution of sulphuretted hydrogen has ceased; the mixture is then poured into a beaker, acidified with hydrochloric acid, to precipitate all the tersulphide of arsenic, as in § 72. The whole is then diluted to, say 300 CC, and 100 CC taken with a pipette, neutralized with carbonate of soda, some bicarbonate added, as in § 64, 1, and the titration for excess of arsenious acid performed with  $\frac{N}{10}$  iodine and starch, as there directed.

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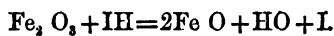
**IODINE. I=127. Free and Combined.**

1 CC or 1 dm.  $\frac{N}{10}$  hyposulphite = 0.0127 Gm. or 0.127 grn. Iodine.  
 " " " = 0.016611 Gm. or 0.16611 grn. Iodide of potassium.

## 1. By Distillation.

§ 67. FREE iodine is of course very readily estimated by solution in iodide of potassium, and titration with starch and  $\frac{N}{10}$  hyposulphite, as described in § 45, 5.

Combined iodine, however, in haloid salts, such as the alkaline iodides, must be subjected to distillation with hydrochloric acid, and some other substance capable of assisting in the liberation of free iodine, which is received into a solution of iodide of potassium, and then titrated with  $\frac{N}{10}$  hyposulphite, in the ordinary way. Such a substance presents itself best in the form of peroxide of iron, or some of its combinations; if, therefore, hydriodic acid, or what amounts to the same thing, an alkaline iodide, be mixed with an excess of peroxide of iron, and distilled in the apparatus shewn in Fig. 16, the following reaction occurs:—



The best form in which to use the oxide of iron is the double sulphate of peroxide of iron, and ammonia or potash, (iron alum.)

The iodide and iron alum being brought into the little flask, Fig. 16, sulphuric acid, of about 1·3 spec. grav. or so, is added, and the cork carrying the still tube inserted. This tube is not carried into the solution of iodide of potassium in this special case, but within a short distance of it, and the end must not be drawn out to a fine point, as there represented, but cut off straight. The reason for this arrangement is that it is not a chlorine distillation for the purpose of setting iodine free from the iodide solution, as is usually the case, but an actual distillation of iodine, which would speedily choke up the narrow point of the tube, and so prevent the further progress of the operation.

As the distillation goes on, the steam washes the condensed iodine out of the tube into the solution of iodide, which must be present in sufficient quantity to absorb it all. When no



more violet vapours are to be seen in the flask, the operation is ended; but to make sure, it is well to empty the ioduretted solution of iodine out of the condensing tube into a beaker, and put a little fresh iodide solution with starch in, then heat the flask again; the slightest traces of iodine may then be discovered by the occurrence of the blue colour. In case this occurs, the distillation is continued a little while, then both liquids mixed, and titrated with  $\frac{N}{10}$  hyposulphite, as usual.

Perchloride of iron may be used instead of the iron alum, but in that case there is some danger of a portion being carried over, which would set iodine free from the iodide, and so give results too high.

The analysis may be checked by titrating the protoxide of iron in the retort with  $\frac{N}{10}$  permanganate or bichromate.

## 2. Estimation of Combined Iodine by Oxidation, (Golfier Besseyre, and Dupré.)

This wonderfully sharp method of estimating iodine, depends upon its conversion into iodic acid by free chlorine. When a solution of iodide of potassium is treated with successive quantities of chlorine water, first iodine is liberated, then chloride of iodine ( $\text{ICl}$ ) formed; if starch, chloroform, benzole, or bisulphide of carbon be added, the first will be turned blue while any of the others will be coloured intense violet; a further addition of chlorine, in sufficient quantity, produces pentachloride of iodine, ( $\text{I Cl}_5$ ) or rather, as water is present, iodic acid, ( $\text{IO}_3$ ;) no colouration of the above substances are produced by these compounds, and the accuracy with which the reaction takes place has been made use of by Golfier Besseyre, and Dupré, independently of each other, for the purpose of estimating iodine. The former suggested the use of starch, the latter chloroform or benzole, with very dilute chlorine water. Dupré's method is preferable on many accounts.

The following examples are taken from Mohr's "Titrimethode."

30 CC of weak chlorine water were put into a beaker with iodide of potassium and starch, then titrated with  $\frac{N}{100}$  hyposulphite of soda, of which 17 CC were required.

10 CC of solution of iodide of potassium, containing 0.010 Gm. of iodine were put into a stoppered bottle, chloroform added, and the same chlorine water as above delivered in from the burette, with constant shaking, until the red colour of the chloroform had disappeared; the quantity used was 85.8 CC. The excess of chlorine was then ascertained by adding bicarbonate of soda, iodide of potassium, and starch liquor; a slight blue colour occurred; this was removed by  $\frac{N}{100}$  hyposulphite, of which 1.2 CC were used. Now as 30 CC of the chlorine solution required 17 CC, the 85.8 CC required 48.62 CC of hyposulphite; from this, however, must be deducted the 1.2 CC in excess, leaving 47.42 CC  $\frac{N}{100} = 4.742$  CC of  $\frac{N}{10}$  hyposulphite, which multiplied by 0.00211, the one-sixth of  $\frac{1}{1000}$  eq., (1 eq. of iodic acid liberating 6 eq. iodine,) gave 0.010036 Gm. iodine instead of 0.01 Gm.

Mohr suggests an improvement upon this method, which dispenses with the use of chloroform, or other similar agent.

The weighed iodine compound is brought into a stoppered flask and chlorine water delivered from a large burette in excess, that is, until all yellow colour has disappeared; a drop of the mixture brought in contact with a drop of starch liquor produces no blue colour; bicarbonate of soda is then added till the mixture is neutral or slightly alkaline, together with iodide of potassium and starch liquor; the blue colour is then removed by  $\frac{N}{100}$  hyposulphite; the strength of the chlorine water being known, the calculation presents no difficulty.

Mohr obtained by this means 0.010108 Gm. iodine, instead of 0.01 Gm.

**CHLORATES, IODATES, AND BROMATES.**

Chloric acid,  $\text{Cl O}_3=75.46$ . Iodic acid,  $\text{IO}_3=166.98$ .

Bromic acid,  $\text{Br O}_3=120$ .

§ 68. THE compounds of chloric, iodic, and bromic acids may all be determined by distillation or digestion with excess of hydrochloric acid; with chlorates the quantity of acid must be considerably in excess.

In each case 1 eq. of the respective acids or their compounds liberate 6 eq. of chlorine, and consequently 6 eq. of iodine when decomposed in the digestion flask. In the case of distillation, however, iodic and bromic acids only set free 4 eq. iodine, while protochlorides of iodine and bromine remain in the retort. In both these cases digestion is preferable to distillation.

Among these substances chloric acid, in the form of chlorate of potash, is the only body of commercial importance, therefore the following example only is given as a specimen of the accuracy of the method of analysis. 0.2043 Gm. pure chlorate of potash, equal to the sixth part of  $\frac{1}{1000}$  eq., was decomposed by digestion with iodide of potassium and strong hydrochloric acid in the bottle shown in Fig. 17; after the reaction was complete, and the bottle cold, the stopper was removed, and the contents washed out into a beaker; starch added, and 103 CC  $\frac{N}{10}$  hyposulphite delivered in from the burette; then again 23.2 CC of  $\frac{N}{100}$  iodine solution, to reproduce the blue colour; this latter was therefore equal to 2.32 CC  $\frac{N}{10}$  iodine, which deducted from the 105 CC hyposulphite gave 100.68 CC, which multiplied by the factor 0.0020428, gave 0.205 Gm. instead of 0.2043 Gm.

Iodate and bromate of potash gave equally sharp results.

## CHLORINE. CL-35.46.

## Chlorine Gas.

1 CC or 1 dm.  $\frac{N}{10}$  arsenic or hyposulphite of soda solution  
= 0.003546 Gm., or 0.03546 grn. Cl.

1 Litre of Chlorine at 32° Fahr., Bar 30<sup>in</sup> weighs 3.17 Gm.

§ 69. CHLORINE water can be titrated with hyposulphite of soda by adding a measured quantity of it to a solution of iodide of potassium, then delivering the hyposulphite from a burette till the colour of the free iodine has disappeared; or by using an excess of the reducing agent, then starch liquor, and titrating residually with  $\frac{N}{10}$  iodine. When arsenic solution is used for titration, the chlorine water is delivered into a solution of carbonate of soda, excess of arsenic added, then starch liquor and  $\frac{N}{10}$  iodine till the colour appears, or the ioduretted starch paper may be used, § 46.

## COMPOUNDS OF HYPOCHLOROUS ACID.

## Chloride of Lime or Bleaching Powder, Chloride of Soda, &amp;c.

§ 70. THE only substance of importance under this head is the so-called chloride of lime, used in very large quantities for bleaching purposes. The estimation of the free chlorine contained in it presents no difficulty when the arsenic solution is used for titration.

Commercial bleaching powder consists of a mixture in variable proportions of hypochlorite of lime, (the true bleaching agent,) chloride of calcium, and hydrate of lime; it is generally valued and sold in this country by its percentage of chlorine.

The first thing to be done in determining the value of a sample of bleaching powder is to bring it into solution, which is best managed as follows :—

The sample is well and quickly mixed, and 10 Gm. weighed, put into a mortar, a little water added, and the mixture rubbed to a smooth cream ; more water is then stirred in with the pestle, allowed to settle a little while, then poured off into a litre flask, the sediment again rubbed with water ; poured off, and so on repeatedly until the whole of the chloride has been conveyed into the flask without loss, and the mortar washed quite clean ; the flask is then filled to the mark with water, well shaken, and 100 CC of the milky liquid taken out with a pipette, emptied into a beaker, and the  $\frac{N}{10}$  arsenic solution delivered in from a burette until a drop of the mixture taken out with a glass rod and brought in contact with the prepared starch paper, § 46, gives no blue stain.

The starch paper may be dispensed with by adding arsenic solution in excess, then starch liquor, and titrating residually with  $\frac{N}{10}$  iodine till the blue colour appears, the number of CC of arsenic used, multiplied by the factor 0.003546, will give the percentage of chlorine.

Example: 100 CC of chloride of lime liquid prepared as above directed were put into a beaker, and 86 CC of arsenic solution added, then starch liquor and 1.5 CC of  $\frac{N}{10}$  iodine to produce the blue colour=84.5 CC of arsenic solution, which multiplied by 0.003546 gave 0.2996 ; and as 1 Gm. of the sample was contained in the 100 CC, 29.96 per cent. of chlorine.

Another 100 CC was carefully titrated with arsenic solution by the aid of iodized starch paper. 84.5 CC were required, also equal to 29.96%. Some recommend that the mixture of chloride of lime and water should be allowed to stand till clear, and the clear liquid only used for titration ; but this invariably gives lower results than when the milky mixture is used.

Instead of weighing 10 Gm. of the sample, and using a CC burette, 100 grains may be weighed, diluted to 10,000 grains,

and 1,000 grains of the liquid=100 dm. taken for titration; the arsenic solution is then delivered from a decem burette; the number of decems used multiplied by the factor 0·03546, will be the percentage of chlorine.

By weighing 3·55 Gm. or 35·5 grn. of the sample, and diluting to 1 litre or 10,000 grains respectively; then taking 100 CC or dm. for titration, the number of CC or dm. of arsenic solution required will be the percentage of chlorine direct.

**Bunsen's Method, (results accurate.)**

10 or 20 CC of the chloride of lime solution, prepared as above, are measured into a beaker, and an excess of solution of iodide of potassium added; the mixture is then diluted somewhat, acidified with hydrochloric acid, and the liberated iodine titrated as in § 45. 1 eq. iodine so found represents 1 eq. chlorine.

**SULPHUR. S-16.**

§ 71.

Substance.	Formula.	Atomic Weight.	$\frac{N}{16}$ Factor.
Sulphuretted Hydrogen ...	H S	17	0·0017
Sulphurous Acid .....	S O <sup>2</sup>	32	0·0032
Hyposulphurous Acid .....	S <sub>2</sub> O <sub>3</sub>	48	0·0048
Hyposulphite of Soda .....	Na O, S <sub>2</sub> O <sub>3</sub> +5HO	124	0·0124

1. When sulphuretted hydrogen is brought in contact with solution of iodine, hydriodic acid is formed, and sulphur set free. (HS + I = IH + S.)

If the solutions are concentrated, however, a peculiar reddish colour occurs which hinders the correct ending of the reaction with starch; the mixture must therefore be diluted freely with freshly boiled and cooled water; the results are not very satisfactory. The determination of sulphuretted hydrogen is on this account preferably made with  $\frac{N}{10}$  arsenious acid solution, described in § 46.

Sulphurous acid is very readily and very accurately estimated by  $\frac{N}{10}$  iodine and starch, as also sulphites and hyposulphites. In the case of solution of sulphurous acid, however, the dilution must be such that not more than 0.04 per cent. of  $\text{SO}_2$  is present. The solutions of sulphites and hyposulphites need not be so much diluted. For the details of the reaction with hyposulphurous and sulphurous acids see § 45. In the determination of hyposulphites, double the atomic weight must be taken, (expressed in centigrammes,) in order that 1 CC of  $\frac{N}{10}$  iodine solution shall be equal to 1 per cent. of substance.

## 2. Estimation of Sulphur in Pyrites, Ores, Residues, &c.

a. By conversion into sulphuric acid, and titration with chloride of barium.

The very finely powdered substance is introduced into a dry flask, together with about three or four times its weight of powdered chlorate of potash, and small quantities of hydrochloric acid added from time to time, the mixture being finally warmed gently till all the sulphur has disappeared by being oxidised into sulphuric acid; the liquid is then diluted, filtered, and titrated as in § 28.

Or the substance may be fused with a mixture of carbonates of potash and soda, and chlorate of potash; the residue lixiviated with boiling water, filtered and titrated as above.

The use of nitrate of potash should be avoided, lest the precipitate of sulphate of baryta should be contaminated with nitrate of baryta.

**5. Alkalimetric Method, (Pelouze.)**

This process, which is more especially designed for the rapid estimation of sulphur in iron and copper pyrites, is susceptible of very tolerable accuracy, the greatest variation from the truth not exceeding 1 or  $1\frac{1}{2}$  % when the manipulation is carefully performed.

The principle of the process is based on the fact that when sulphur is ignited with chlorate of potash and carbonate of soda, the sulphur is converted by oxidation entirely into sulphuric acid, which expels its equivalent proportion of carbonic acid from the soda, forming neutral sulphate of soda; if, therefore, an accurately weighed quantity of the substance be fused with a known weight of pure carbonate of soda in excess, and the resulting mass titrated with normal acid, to find the quantity of unaltered carbonate of soda, the proportion of sulphur is readily calculated from the difference between the volume of normal acid required to saturate the original carbonate of soda, and that actually required after the ignition.

For the sake of avoiding calculation, it is advisable to take 1 Gm. of the finely levigated pyrites, and 5.3 Gm. of pure carbonate of soda for each assay; and as 5.3 Gm. carbonate of soda represent 100 CC of normal sulphuric acid, ( $=4.0$  Gm.  $\text{SO}_2$ ), it is only necessary to subtract the number of CC used after the ignition from 100, and multiply the remainder by the factor 0.016, (1 CC normal acid being equal to 0.016 Gm. S.) in order to arrive at the weight of sulphur in the 1 Gm. of pyrites, and by moving the decimal point two places to the right, the percentage of that substance is obtained.

An example will shew the details of the process and calculation.

Some cubes of iron pyrites were broken, and a small portion very finely powdered in a hardened steel mortar.

1 Gm. of the powder was mixed *intimately* with 5.3 Gm. pure carbonate of soda, and about 7 Gm. each of chlorate of



potash, and decrepitated chloride of sodium, in powder, (the latter is added for the purpose of moderating the action,) the whole was then introduced into a platinum crucible, and gradually exposed to a dull red heat for ten minutes; the crucible was then suffered to cool somewhat, and warm distilled water added; the solution so obtained was drawn off with a pipette and brought on a moistened filter, the process repeated five or six times, the residue then emptied into a beaker and boiled with a large quantity of water, the whole brought on the filter and thoroughly washed with boiling water till all soluble matter was removed; the clear filtrate was then coloured with litmus, and titrated as in §§ 12, 13. 67 CC of normal acid were required, which deducted from 100 left 33 CC, this multiplied by 0.016 gave 0.528 Gm. sulphur, or 52.8 %; pure  $\text{Fe S}_2$  contains 53.3 %.

The insoluble oxide of iron remaining on the filter was dissolved in hydrochloric acid, and titrated with bichromate of potash, as in § 44, yielding 46.5 % iron; the determination of both substances occupied less than an hour, and the loss, supposing the pyrites to be pure, amounted to less than  $\frac{1}{4}$  of a per cent.

If pure carbonate of soda is not at hand, the ordinary commercial article will answer the purpose, but the quantity of normal acid necessary to saturate it must of course be previously found. An iron spoon or ladle may also be used instead of the platinum crucible.

If roasted pyrites is to be examined by this method, it is unnecessary to add the salt, and equal quantities of the substance, carbonate of soda and chlorate of potash may be taken for the combustion.

If the grain system of weights and measures are used, the quantity of pyrites will be 10 grains, and of carbonate of soda 53 grains, each decem of normal acid being equal to 0.16 grn. sulphur.

It is not of course absolutely necessary that these quantities should be used, but less calculation is needed by this plan than any other.

**SULPHURETTED HYDROGEN. HS = 17.**

1 CC  $\frac{N}{10}$  arsenious acid = 0.00255 Gm. HS.

1 dm.           ,,       ,, = 0.0255 grn. ,,

**Mohr's Method, (results accurate.)**

§ 72. THIS residual process is far preferable to the direct titration of sulphuretted hydrogen by iodine, as devised by Dupasquier. The principle is based on the fact that when sulphuretted hydrogen is brought in contact with an excess of arsenious acid in solution, tersulphide of arsenic is formed; 1 eq. arsenious acid and 3 eq. sulphuretted hydrogen produce 1 eq. tersulphide of arsenic and 3 eq. water,



The excess of arsenious acid used, is found by  $\frac{N}{10}$  iodine and starch, as in § 46, 2. In the case of estimating the strength of sulphuretted hydrogen water, the following plan may be pursued.

A measured quantity, say 10 CC  $\frac{N}{10}$  arsenic solution, is put into a 300 CC flask, and 20 CC sulphuretted hydrogen water added, well mixed, and sufficient hydrochloric acid added to produce a distinct acid reaction, this produces a precipitate of tersulphide of arsenic, and the liquid itself is colourless. The whole is then diluted to 300 CC, filtered through a dry filter into a dry vessel, 100 CC of the filtrate taken out and neutralized with bicarbonate of soda, then titrated with  $\frac{N}{10}$  iodine and starch, as in § 64, 1, the quantity of arsenious acid so found is deducted from the original 10 CC, and the remainder multiplied by the requisite factor for sulphuretted hydrogen.

The estimation of sulphuretted hydrogen contained in carburetted hydrogen gas, can by this method be made very accurately by leading the gas through the arsenic solution, or still better, through a dilute solution of caustic alkali, then adding arsenic solution, and titrating as before described. The

apparatus devised by Mohr for this purpose is arranged as follows. The gas from a common burner is led by means of a vulcanized tube into two successive small wash bottles, containing the alkaline solution; from the last of these it is led into a large Woulff's bottle, filled with water, the bottle has two necks, and a tap at the bottom, one of the necks contains the cork through which the tube carrying the gas is passed; the other, a cork through which a good-sized funnel with a tube reaching to the bottom of the bottle is passed; when the gas begins to bubble through the flasks, the tap is opened so as to allow the water to drop rapidly; if the pressure of gas is strong, the funnel tube acts as a safety valve, and allows the water to rise up into the cup of the funnel; when a sufficient quantity of gas has passed into the bottle, say six or eight pints, the water which has issued from the tap into some convenient vessel, is measured into cubic inches or litres, and gives the quantity of gas which has displaced it. In order to insure accurate measurement, all parts of the apparatus must be tight.

The flasks are then separated, and into the second, 5 CC of arsenic solution placed, and acidified slightly with hydrochloric acid; if any traces of a precipitate occur, it is set aside for titration with the contents of the first flask, into which 10 CC or so of arsenic are put, acidified as before, both mixed together, diluted to a given measure, filtered, and a measured quantity titrated as before described.

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#### INDIGO.

Factor for  $\frac{N}{10}$  permanganate or  
 bichromate ..... 0.00752 Gm., or 0.0752 grn.

§ 73. THE estimation of indigo is a purely technical affair, and does not belong to scientific analysis; nevertheless, it is a

substance most largely and successfully adulterated, so far as the eye is concerned, and frequently needs examination by chemical means. The factors given above would lead one to suppose that the article was as definite in composition as Epsom salts or any other substance known to be combined in strict chemical proportions; this, however, is not the case with indigo; as it never occurs in commerce pure. The factors given above are calculated from the examination of the purest indigo that can be obtained by chemical means; that is, by the reduction and oxidation of the pure colouring matter contained in the commercial article.

The determination of the true value of any sample of commercial indigo by chemical analysis requires great care and considerable practice.

The processes here given are those which seem on the whole preferable, but they are by no means so sharp and secure in their results as could be wished.

1. Mohr's method consists in dissolving a weighed quantity of the material in sulphuric acid, diluting the solution and titrating with permanganate of potash until all the blue or green colour has disappeared, and gives place to a dirty yellow shade; at this point all the real indigo blue is oxidised; if more permanganate be added, its colour will be removed in consequence of the presence of other matters which decompose it; therefore the appearance of the rose colour cannot be taken as the end of the process, as is the case in other analyses by that substance; repeated and careful practice has shown that the plan is reliable when the occurrence of the brownish yellow colour is taken as the end of the titration.

The greatest care is necessary in preparing the solution of indigo for titration. The following plan is recommended as the best:—One gramme or 10 grains respectively of the finely-powdered sample is weighed and put into a stoppered flask, holding about three or four ounces, with a small handful of clean flint pebbles, about the size of swan shot; both well

shaken together, and about 8 or 10 CC or dm. of fuming Nordhausen sulphuric acid added, the stopper inserted, and the whole mixed by shaking. The flask is then put into a slightly warm place, about 70° Fahr., for six or eight hours, occasionally shaking; water is then added, and the liquid decanted into a litre or 10,000 grain flask, according to circumstances; the flints repeatedly washed, and the washings added to the first liquid until they are clean and the measure made up. 100 CC or dm. of this well-mixed solution are then removed with a pipette, diluted with three or four times its volume of water, and titrated with permanganate (constantly agitating the liquid) from a CC or dm. burette, as the case may be, until the last traces of green colour have disappeared, and the brownish yellow only remains. As there is sufficient solution for several other titrations, the results can be checked, but it must be borne in mind that the same amount of dilution, or thereabouts, must be used, or the results will vary.

The quantity of permanganate so used is calculated for the whole quantity of indigo taken, reduced to  $\frac{N}{10}$  strength, if not already so, and multiplied by the necessary factor.

## 2. Penny's Process.

The solution of indigo is prepared precisely as before described; but instead of permanganate, bichromate of potash with hydrochloric acid is used for the titration.

100 CC or dm. of the indigo solution is mixed with about 5 CC or dm. of strong and pure hydrochloric acid and a little water in a porcelain capsule, gently heated, and  $\frac{N}{10}$  bichromate delivered from the burette, keeping the mixture well stirred, until a drop of the liquid taken out with a glass rod and put upon filtering paper gives a light brown stain, without any admixture of blue or green. The end of the reaction is somewhat difficult to distinguish, but considerable practice will overcome this difficulty.

The calculation is the same as with  $\frac{N}{10}$  permanganate.

Schlumberger's method consists in adding the indigo solution prepared as above to a measured quantity of solution of chloride of lime, the strength of which has just previously been determined by a solution of pure indigo blue; but as this is a most expensive and rare material, and must be used for almost every analysis, the process will not be further described.

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## PART IV.

## ANALYSIS BY PRECIPITATION.

## INTRODUCTION.

THE general principle of this method of determining the quantity of any given substance is alluded to in § 1, and in all instances is such that the body to be estimated forms an insoluble precipitate with a titrated re-agent. The end of the reaction is however determinable in three ways.

1. By adding the re-agent until no further precipitate occurs, as in the determination of chlorine by silver.

2. By adding the re-agent in the presence of an indicator contained either in the liquid itself, or brought externally in contact with it; so that the slightest excess of the re-agent shall produce a characteristic reaction with the indicator, as in the estimation of silver with salt, by the aid of chromate of potash, or that of phosphoric acid with uranium by yellow prussiate of potash.

3. By adding the re-agent to a clear solution until a precipitate occurs, as in the estimation of cyanogen by silver.

The first of these endings can only be applied with great accuracy to silver and chlorine estimations. Very few precipitates have the peculiar quality of chloride of silver, namely,

perfect insolubility, and the tendency to curdle closely by shaking, so as to leave the menstruum clear; some of the most insoluble precipitates, such as sulphate of baryta and oxalate of lime, are unfortunately excluded from this class, because their finely-divided or powdery nature prevents their ready and perfect subsidence.

In all these cases, therefore, it is necessary to find an indicator, which brings them into class 2.

The third class comprises only two substances, viz., the determination of cyanogen by silver, and that of chlorides by nitrate of mercury.

CHLORINE. CL=35.46.

1 CC or 1 dm.	$\frac{N}{10}$	silver solution	= 0.003546 Gm. or 0.03546 grn.
		Chlorine	
"	"	"	= 0.005846 Gm. or 0.05846 grn.
		Chloride of Sodium	

§ 74. THE powerful affinity existing between chlorine and silver in solution, and the ready precipitation of the resulting chloride, seem to have led to the earliest important volumetric process in existence, viz., the determination of silver by the wet method devised by Gay Lussac. The details of the process are more particularly described under the article relating to the assay of silver; the determination of chlorine is just the converse of the process there described, and the same precautions, and to a certain extent the same apparatus, are required.

The solutions required, however, are systematic; and for exactness and convenient dilution are of decinormal strength.



**The Decinormal Solution of Silver.**

10.797 Gm. of pure silver, § 76, 3, *b*, are dissolved in pure nitric acid with gentle heat in a flask, into the neck of which a small funnel is dropped to prevent loss of liquid by spiriting; when solution is complete, the funnel must be washed inside and out with distilled water into the flask, and the liquid diluted to 1 litre; or if it be desired to use chromate of potash as indicator in any analysis, the solution must be neutral; in which case the solution of silver in nitric acid is evaporated to dryness, and the residue dissolved in 1 litre; or, what is preferable, 16.997 Gm. of pure and dry recrystallized nitrate of silver is dissolved in 1 litre of distilled water. If the grain system is used, 107.97 grn. silver or 169.97 grn. nitrate is dissolved, and the solution diluted to 10,000 grains.

**The Decinormal Solution of Salt.**

5.846 Gm. pure chloride of sodium, § 76, 3, *a*, are dissolved in distilled water, and the solution made up to 1 litre, or 58.46 grn. to 10,000 grains.

There are two methods by which the analysis may be ended—

*a*. By adding silver cautiously, and well shaking after each addition till no further precipitate is produced.

*b*. By using a few drops of solution of chromate of potash as indicator, as devised by Mohr.

For the ending *a* refer to § 76, 3.

The ending *b* is exceedingly serviceable, on the score of saving both time and trouble. There are conditions, however, attached to its use, which must not be disregarded. The most important of these is that the solutions must be absolutely free from acid or any great excess of alkali; it is best to have them neutral. When, therefore, acid is present in any solution to

be examined, it should be neutralized with carbonate of soda ; a slight excess of this substance is not of much consequence ; an excess of caustic alkali must not be permitted, as in that case oxide of silver would be formed.

#### The Analytical Process.

To the neutral or faintly alkaline solution containing chlorine, four or five drops of a cold saturated solution of yellow chromate of potash is added, and the silver solution delivered from the burette until the last drop or two produce a permanent blood-red colour, an evidence that all the chlorine has entered into combination with the silver, and the drop or two in excess has formed a precipitate of chromate of silver ; the reaction is very delicate and easily distinguished.

Example : 1 Gm. pure chloride of sodium was dissolved in water, a few drops of chromate solution added, and titrated with  $\frac{N}{10}$  silver, of which 17.14 CC were required to produce the red colour ; multiplied by the  $\frac{N}{10}$  factor for chloride of sodium = 0.005846, the result was 1.002 Gm. Na Cl, instead of 1 Gm.

The determination of chlorides by Liebig's method, with nitrate of mercury, is described in § 80, 2.

**INDIRECT ESTIMATION OF AMMONIA, SODA, POTASH, LIME, AND OTHER ALKALIES AND ALKALINE EARTHS, WITH THEIR CARBONATES, NITRATES, AND CHLORATES, ALSO NITROGEN, &c., BY MEANS OF DECINORMAL SILVER SOLUTION.**

1 CC  $\frac{N}{10}$  silver solution =  $\frac{1}{100.000}$  eq. of each substance.

§ 75. MOHR, with his characteristic ingenuity, has made use of the delicate reaction between chlorine and silver, with

chromate of potash as indicator, for the determination of the bodies mentioned above. All compounds capable of being converted into neutral chlorides by evaporation to dryness with hydrochloric acid, may be determined with great accuracy. The chlorine in a combined state is of course the only substance actually determined, but as the laws of chemical combination are exact and well known, the measure of chlorine is also the measure of the base with which it is combined.

*a.* In most cases it is necessary only to slightly supersaturate the alkali, or its carbonate, with pure hydrochloric acid; evaporate on the water bath to dryness, and heat for a time to 250° Fahr. in the air bath, then dissolve to a given measure, and take a portion for titration.

*b.* Alkalies and Earths with organic acids are ignited to convert them into carbonates, then treated with hydrochloric acid, and evaporated as before.

*c.* Carbonic Acid in combination may be determined by precipitation with chloride of barium, as in § 22 *a*, the washed precipitate is dissolved on the filter with hydrochloric acid, (covering it with a watch-glass to prevent loss,) then evaporated to dryness. In order to titrate with accuracy by the help of the chromate of potash, the baryta must be precipitated by means of a solution of pure sulphate of soda or potash, added in slight excess; the precipitated sulphate of baryta does not interfere with the delivery of the reaction; if this precaution were not taken the yellow chromate of baryta would mislead.

*d.* Free Carbonic Acid is collected by means of ammonia and chloride of barium, as in § 22 *b*, and the estimation completed as in *c*.

*e.* Chlorates are converted into chlorides by ignition, then titrated with  $\frac{N}{10}$  silver and chromate.

*f.* Nitrates are evaporated with concentrated hydrochloric acid, and the resulting chlorides titrated as *e*.

*g.* Nitrogen. The ammonia evolved from guano, manures, oilcakes, and sundry other substances, when burned with soda

lime in Will and Varrentrapp's apparatus, is conducted through dilute hydrochloric acid; the liquid evaporated to dryness, and titrated as in *e*.

In all cases the operator will of course take care that no chlorine from extraneous sources but the hydrochloric acid is present, or if it exists in the bodies themselves as an impurity, its quantity must be first determined.

Example: 0.25 Gm. pure carbonate of soda was dissolved in water, and hydrochloric acid added till in excess; then dried on the water-bath till no further vapours of acid were evolved; the resulting white mass was heated for a few minutes to about 240° Fahr., dissolved and made up to 300 CC; 100 CC required 15.7 CC  $\frac{N}{10}$  silver, this multiplied by 3 gave 47.1 CC, which multiplied by the  $\frac{N}{10}$  factor for carbonate of soda, = 0.0053, gave 0.24963 Gm. instead of 0.25 Gm.

*h*. Indirect Estimation of Potash and Soda existing as Mixed Chlorides.

It is a problem of frequent occurrence to find the relative quantities of potash and soda existing in mixtures of the two alkalis; such as occur, for instance, in urine, manures, soils, waters, &c. The actual separation of potash from soda by means of bichloride of platinum is tedious, and not always satisfactory.

The following method of calculation is frequently convenient, since a careful estimation of the chlorine present in the mixture is the only labour required, and which can most readily be accomplished by  $\frac{N}{10}$  silver and chromate of potash, as previously described.

1. The weight of the mixed pure chlorides is accurately found and noted.

2. The chlorides are then dissolved in water, and very carefully titrated with  $\frac{N}{10}$  silver and chromate of potash for the amount of chlorine present, which is also recorded; the calculation is then as follows:—

The weight of chlorine is multiplied by the factor 2.1029,

from the product so obtained is deducted the weight of the mixed salts found in 1. The remainder multiplied by 0.36288 will give the weight of chloride of sodium present in the mixture.

The weight of chloride of sodium deducted from the total as found in 1, will give the weight of chloride of potassium.

Chloride of sodium  $\times 0.5302 = \text{Soda, (NaO.)}$

Chloride of potassium  $\times 0.6317 = \text{Potash, (KO.)}$

The principle of the calculation, which is based on the atomic constitution of the individual chlorides, is explained in most of the standard works on general analysis.

#### SILVER. Ag—107.97.

1 CC or 1 dm.  $\frac{N}{10}$  solution of chloride of sodium = 0.010797 Gm. or 0.10797 grn. metallic silver; also 0.016997 Gm. or 0.16997 grn. nitrate of silver.

**Decinormal Solution of Chloride of Sodium.—See Sect. 74.**

**Decinormal Solution of Silver.—See Sect. 74.**

§ 76. THE determination of silver is precisely the converse of the operations just described under chlorine, and the process may either be concluded by adding the chloride of sodium till no further precipitate is produced, or the chromate of potash may be used as indicator. In the latter case, however, it is advisable to add the chloride solution in excess, then a drop or two of chromate solution, and titrate residually with  $\frac{N}{10}$  silver solution, till the red colour is produced, for the excess of chloride of sodium.

### 1. Analysis of the Silver Solutions used in Photography.

The silver bath solutions for sensitizing collodion and paper frequently require examination, as their strength is constantly lessening. To save calculation, it is better to use an empirical solution of salt than the systematic one described above.

This is best prepared by dissolving 43 grains of pure chloride of sodium in 10,000 grains of distilled water; each decem (=10 grs.) of this solution will precipitate 0.125 grn. (i.e.  $\frac{1}{8}$  grn.) of pure nitrate of silver, therefore if 1 fluid drachm of any silver solution be taken for examination, the number of decems of salt solution required to precipitate all the silver will be the number of grains of nitrate of silver in each ounce of the solution.

Example: One fluid drachm of an old nitrate of silver bath was carefully measured into a stoppered bottle, 10 or 15 drops of pure nitric acid and a little distilled water added; the salt solution was then cautiously added, shaking well after each addition until no further precipitate was produced, the quantity required was 26.5 dm., =  $26\frac{1}{2}$  grains of nitrate of silver in each ounce of solution.

Crystals of nitrate of silver may also be examined in the same way, by dissolving say 30 or 40 grs. in an ounce of water, taking one dram of the fluid and titrating as above.

In consequence of the rapidity and accuracy with which silver may be determined, when chromate of potash is used as indicator, some may prefer to use that method. It is then necessary to have a standard solution of silver, of the same chemical power as the salt solution; this is made by dissolving 125 grains of pure and dry neutral nitrate of silver in 10,000 grs. of distilled water; both solutions will then be equal, volume for volume.

Suppose, therefore, it is necessary to examine a silver solution used for sensitizing paper. One dram is measured, and if any free acid is present, cautiously neutralized with a weak solution

of carbonate of soda; 100 dm. of salt solution is then added with a pipette, if the solution is under 100 grs. to the ounce the quantity will be sufficient. 3 or 4 drops of solution of chromate of potash are then put in, and the silver solution delivered from the burette until the blood-red colour of chromate of silver is just visible. Suppose that 25.5 dm. have been required, let that number be deducted from the 100 dm. of salt solution, which will leave 74.5 dm., or  $74\frac{1}{2}$  grains to the ounce.

This method is much more likely to give exact results in the hands of persons not expert in analysis than the ordinary plan by precipitation, inasmuch as with collodion baths, containing as they always do iodide of silver, it is almost impossible to get the supernatant liquid clear enough to distinguish the exact end of the analysis.

**2. Estimation of Silver, in Ores and Alloys, by Iodide of Starch.**  
**Methods of Pisani and F. Field, (very accurate in the absence of mercury, protoxides, and salts of tin, iron, and manganese, antimony, arsenious acid, and chloride of gold.)**

If a solution of the blue iodide of starch be added to a neutral solution of nitrate of silver, while any of the latter is in excess the blue colour disappears, the iodine entering into combination with the silver; as soon as all the silver is thus saturated the blue colour remains permanent and marks the end of the process; the reaction is very delicate, and the process accurate in the absence of the metals and salts mentioned above, it is more especially applicable to the analysis of ores and alloys of silver containing lead and copper.

The solution of iodide of starch devised by Pisani, is made by rubbing together in a mortar 2 Gm. iodine with 15 Gm. of starch and about 6 or 8 drops of water, putting the moist mixture into a stoppered flask and digesting in a water-bath for about an hour or until it has assumed a dark bluish-gray colour, water is then added till all is dissolved. The strength

of the solution is then ascertained by titrating it with 10 CC of a solution of silver containing 1 Gm. in the litre; to which a portion of pure precipitated carbonate of lime is added; the addition of this latter removes all excess of acid, and at the same time enables the operator to distinguish the end of the reaction more accurately. The starch solution should be of such a strength that about 50 CC is required for 10 CC of the silver solution, ( $\approx 0.01$  Gm. silver.)

F. Field, "Chem. News," vol. ii, p. 17,) who discovered the principle of this method simultaneously with Pisani, uses a solution of iodine in iodide of potassium with starch liquor. Those who desire to make use of this plan can use the deci and centinormal solutions of iodine described in the former part of this treatise, the results being the same in either case.

In the analysis of silver containing copper the solution must be considerably diluted in order to weaken the colour of the copper, a small measured portion is then taken, carbonate of lime added, and iodide of starch till the colour is permanent. It is best to operate with about from 60 to 100 CC, containing not more than 0.02 Gm. silver; when the quantity is much greater than this it is preferable to precipitate the greater portion with  $\frac{N}{10}$  chloride of sodium, and to complete with iodide of starch after filtering off the chloride. When lead is present with silver in the nitric acid solution, add sulphuric acid and filter off the sulphate of lead, then add carbonate of lime to neutralize excess of acid, filter again if necessary, then add fresh carbonate of lime and titrate as above.

**3. Assay of Commercial Silver, (Plate, Bullion, Coin, &c.) Gay  
Lussac's Method modified by J. G. Mulder.**

For more than 30 years Gay Lussac's method of estimating silver in its alloys has been practised intact, at all the European mints under the name of the "humid method," in place of the old system of cupellation; during that time it has



been regarded as one of the most exact methods of quantitative analysis; the researches of Mulder, however, into the innermost details of the process have shewn that it is capable of even greater accuracy than has hitherto been gained by it. For the particulars of Mulder's investigations I cannot do better than refer the reader to the excellent translation of his memoir, published in the "Chemical News," by my friend Dr. Adriani, of Edinburgh.

The principle of the process is the same as described under the head of chlorine, depending on the affinity which that body has for silver in preference to all other substances, and resulting in the formation of chloride of silver, a compound insoluble in dilute acids, and which readily separates itself from the liquid in which it is suspended.

The plan originally devised by the illustrious inventor of this process for assaying silver and which is still followed, is to consider the weight of alloy taken for examination to consist of 1000 parts, and the question is to find how many of these parts are pure silver. This empirical system was arranged for the convenience of commerce, and being now thoroughly established it is the best plan of procedure; if, therefore, a standard solution of salt be made of such strength that 100 CC will exactly precipitate 1 gramme of silver, it is manifest that each  $\frac{1}{10}$  CC will precipitate 1 milligramme or  $\frac{1}{1000}$ th part of the gramme taken, and, consequently in the analysis of 1 gramme of any alloy containing silver, the number of  $\frac{1}{10}$  CC required to precipitate all the silver out of it would be the number of thousandths of pure silver contained in the specimen.

In practice, however, it would not do to follow this plan precisely, inasmuch as neither the measurement of the standard solution nor the ending of the process would be gained in the most exact manner, consequently a decimal solution of salt, one-tenth the strength of the standard solution, is prepared, so that 1000 CC will exactly precipitate 1 gramme of silver, and, therefore, 1 CC one milligramme.

The silver alloy to be examined, (the composition of which must be approximately known,) is weighed so that about 1 gramme of pure silver is present, it is then dissolved in pure nitric acid by the aid of a gentle heat, and 100 CC of standard solution of salt added from a pipette in order to precipitate exactly 1 Gm. of silver, the bottle containing the mixture is then well shaken until the chloride of silver has curdled, leaving the liquid clear.

The question is now—Which is in excess, salt or silver? A drop of decimal salt solution is added, and if a precipitate is produced, 1 CC is delivered in, and after clearing, another, and so on as long as a precipitate is produced; if on the other hand the one drop of salt produced no precipitate, showing that the pure silver present was less than 1 Gm., a decimal solution of silver is used, prepared by dissolving 1 Gm. pure silver in pure nitric acid and diluting to 1 litre, this solution is added after the same manner as the salt solution just described, until no further precipitate occurs; in either case the quantity of decimal solution used is noted, and the results calculated in thousandths for 1 Gm. of the alloy.

The process thus shortly described is that originally devised by Gay Lussac, and it was taken for granted that when equivalent chemical proportions of silver and chloride of sodium were brought thus in contact that every trace of the metal was precipitated from the solution, leaving nitrate of soda and free nitric acid only in solution. The researches of Mulder, however, go to prove that this is not strictly the case, but that when the most exact chemical proportions of silver and salt are made to react on each other, and the chloride has subsided, a few drops more of either salt or silver solution will produce a further precipitate, indicating the presence of both nitrate of silver and chloride of sodium in a state of equilibrium, which is upset on the addition of either salt or silver. Mulder decides, and no doubt rightly, that this peculiarity is owing to the presence of nitrate of soda,

and varies somewhat with the temperature and state of dilution of the liquid.

It therefore follows that when a silver solution is carefully precipitated, first by concentrated and then by dilute salt solution, until no further precipitate appears, the clear liquid will at this point give a precipitate with dilute silver solution, and if it be added till no further cloudiness is produced, it will again be precipitable by dilute salt solution.

For example: Suppose that in a given silver analysis the decimal salt solution has been added so long as a precipitate is produced, and that 1 CC (=20 drops of Mulder's dropping apparatus) of decimal silver is in turn required to precipitate the apparent excess, it would be found that when this had been done, 1 CC more of salt solution would be wanted to reach the point at which no further cloudiness is produced by it, and so the changes might be rung time after time; if, however, instead of the last 1 CC (=20 drops) of salt, half the quantity be added, that is to say 10 drops (=  $\frac{1}{2}$  CC); Mulder's so-called neutral point is reached, namely, that in which, if the liquid be divided in half, both salt and silver will produce the same amount of precipitate. At this stage the solution contains chloride of silver dissolved in nitrate of soda, and the addition of either salt or silver expels it from solution.

A silver analysis may therefore be concluded in three ways—

1. By adding decimal salt solution until it just ceases to produce a cloudiness.
2. By adding a slight excess of salt, and then decimal silver till no more precipitate occurs.
3. By finding the neutral point.

According to Mulder the latter is the only correct method, and preserves its accuracy at all temperatures up to  $56^{\circ}$  C (=  $133^{\circ}$  Fahr.) while the difference between 1 and 3 amounts to  $\frac{1}{2}$  a milligramme, and that between 1 and 2 to 1 milligramme on 1 gramme of silver at  $16^{\circ}$  C (=  $62^{\circ}$  Fahr.) and is seriously increased by variation of temperature.

It will readily be seen that much more trouble and care is required by Mulder's method than by that of Gay Lussac, but as a compensation, much greater accuracy is obtained.

On the whole, it appears to me preferable to weigh the alloy so that slightly more than 1 Gm. of silver is present, and to choose the ending No. 1, adding drop by drop the decimal salt solution until just a trace of a precipitate is seen, and which, after some practice, is known by the operator to be final. It will be found that the quantity of salt solution used will slightly exceed that required by chemical computation—say 100.1 CC are found equal to 1 Gm. silver, the operator has only to calculate that quantity of the salt solution in question for every 1 Gm. silver he assays in the form of alloy, and the error produced by the solubility of chloride of silver in nitrate of soda is removed.

If the decimal solution has been cautiously added, and the temperature not higher than 62° Fahr., this method of conclusion is as reliable as No. 3, and free from the possible errors of experiment, for it requires a great expenditure of time and patience to reverse an assay two or three times, and each time cautiously adding the solutions, drop by drop, then shaking and waiting for the liquid to clear, beside the risk of discolouring the chloride of silver, which would at once vitiate the results.

The decimal silver solution, according to this arrangement, would seldom be required; if the salt has been incautiously added, or the quantity of alloy too little to contain 1 Gm. pure silver, then it is best to add once for all 2, 3, or 5 CC, according to circumstances, and finish with decimal salt as No. 1, deducting the silver added.

#### **The Standard Solutions and Necessary Apparatus.**

*a.* Standard Solution of Salt. Pure chloride of sodium is prepared by treating a concentrated solution of the

whitest table salt first with a solution of caustic baryta to remove sulphuric acid and magnesia, then with a slight excess of carbonate of soda to remove baryta and lime, warming and allowing the precipitates to subside; then evaporating to a small bulk, that crystals may form; these are separated by a filter, and slightly washed with cold distilled water; dried, removed from the filter, and heated to dull redness, and when cold preserved in a well-closed bottle for use. The mother liquor is thrown away or used for other purposes. Of the salt so prepared, or of chemically pure rock-salt (Steinsalz, a substance to be obtained freely in Germany) 5·4145 Gm. is to be weighed and dissolved in 1 litre of distilled water at 62° Fahr. 100 CC of this solution will precipitate exactly 1 Gm. silver; it is preserved in a well-stoppered bottle, and shaken before use.

**Decimal Solution of Salt.** 100 CC of the above solution is diluted to exactly 1 litre with distilled water at 62° Fahr. 1 CC will precipitate 0·001 Gm. silver.

**b. Decimal Solution of Silver.** Pure metallic silver is best prepared by galvanic action from pure chloride; and as clean and secure a method as any, is to wrap a lump of clean zinc, into which a silver wire is melted, with a piece of wetted bladder or calico, so as to keep any particles of impurity contained in the zinc from the silver. The chloride is placed at the bottom of a porcelain dish, covered with dilute sulphuric acid, and the zinc laid in the middle; the silver wire is bent over so as to be immersed in the chloride; as soon as the acid begins to act upon the zinc, the reduction commences in the chloride and grows gradually all over the mass; the resulting finely-divided silver is well washed, first with dilute acid, then with hot water, till all acid and soluble zinc are removed.

The moist metal is then mixed with a little carbonate of soda, saltpetre, and borax, say about an eighth part of each, and dried perfectly.

The metallic silver obtained as above is never free altogether from organic matter and undecomposed chloride, and, therefore, it must invariably be melted. Mulder recommends that the melting should be done in a porcelain crucible, immersed in sand contained in a common earthen crucible; borax is sprinkled over the surface of the sand so that it may be somewhat vitrified, that in pouring out the silver when melted no particles of dirt or sand may fall into it. If the quantity of metal is small it may be melted in a porcelain crucible over a gas blow-pipe.

The molten metal obtained in either case can be poured into cold water and so granulated, or upon a slab of pipe-clay, into which a glass plate has been pressed when soft so as to form a shallow mould. The metal is then washed well with boiling water to remove accidental surface impurities, and rolled into thin strips by a goldsmith's mill, in order that it may be readily cut for weighing; the granulated metal is, of course, ready for use at once without any rolling.

1 Gm. of this silver is dissolved in pure dilute nitric acid and diluted to 1 litre—each CC contains 0.001 Gm. silver—it should be kept from the light.

**Dropping Apparatus for concluding the Assay.** Mulder constructs a special affair for this purpose, consisting of a pear-shaped vessel fixed in a stand, with special arrangements for preventing any continued flow of liquid, the delivery tube has an opening of such size that 20 drops measure exactly 1 CC—the vessel itself is not graduated. As this arrangement is of more service to assay than to general laboratories, it need not be further described here. A small burette divided in  $\frac{1}{10}$  CC with a convenient dropping tube will answer every purpose, and possesses the further advantage of recording the actual volume of fluid delivered.

The 100 CC pipette, for delivering the concentrated salt solution, must be accurately graduated, and should deliver exactly 100 Gm. of distilled water at 62 Fahr.

The test bottles, holding about 200 CC, should have their stoppers well ground and brought to a point, and should be fitted into japanned tin tubes reaching as high as the neck, so as to preserve the precipitated chloride from the action of light, and, when shaken, a piece of black cloth should be covered over the stopper.

c. Titration of the Standard Salt Solution. From what has been said previously as to the principle of this method, it will be seen that it is not possible to rely absolutely upon a standard solution of salt, containing 5.4145 Gm. per litre, although this is chemically correct in its strength. The real working power must be found by experiment. From 1.002 to 1.004 Gm. of absolutely pure silver is weighed on the assay balance, put into a test bottle with about 5 CC of pure nitric acid about 1.2 spec. grav., and gently heated in the water or sand bath till it is all dissolved. The nitrous vapours are then blown from the bottle, and it is set aside to cool down to about 62° Fahr.

The 100 CC pipette, which should be securely fixed in a support, is then carefully filled with the salt solution, and delivered into the test bottle contained in its case, the moistened stopper inserted, covered over with the black velvet or cloth, and shaken continuously till the chloride has clotted and the liquid becomes clear; the stopper is then slightly lifted and its point touched against the neck of the bottle to remove excess of liquid, again inserted, and any particles of chloride washed down from the top of the bottle by carefully shaking the clear liquid over them. The bottle is then brought under the decimal salt burette, and  $\frac{1}{2}$  CC added, the mixture shaken, cleared, another  $\frac{1}{2}$  CC put in, and the bottle lifted partly out of its case to see if the precipitate is considerable; lastly, 2 or 3 drops only of the solution are added at a time until no further opacity is produced by the final drop. Suppose, for instance, that in titrating the salt solution it is found that 1.003 Gm. silver require 100 CC concentrated, and 4 CC decimal solution, altogether equal to 100.4 CC concentrated, then—

1.003 silver : 100.4 salt :: 1.000 :  $x$   $x=100.0999$ .

The result is within  $\frac{1}{100,000}$  of 100.1, which is near enough for the purpose and may be more conveniently used. The operator therefore, knows that 100.1 CC of the concentrated salt solution at 62° Fahr. will exactly precipitate 1 Gm. silver, and calculates accordingly in his examination of alloys.

In the assay of coin and plate of the English standard, namely, 11.1 silver and 0.9 copper, the weight corresponding to 1 Gm. silver is 1.081 Gm., therefore, in examining this alloy 1.085 Gm. may be weighed.

When the quantity of silver is not approximately known, a preliminary analysis is necessary, which is best made by dissolving  $\frac{1}{2}$  or 1 Gm. of the alloy in nitric acid, and precipitating very carefully with the concentrated salt solution from a  $\frac{1}{10}$  CC burette. Suppose that in this manner 1 Gm. of alloy required 45 CC salt solution,

100.1 salt : 1.000 silver :: 45 :  $x$   $x=0.4495$ , and again

0.4495 : 1 :: 1.003 :  $x=2.231$ .

2.231 Gm. of this particular alloy are therefore taken for the assay.

Where alloys of silver contain sulphur or gold, with small quantities of tin, lead, or antimony, they are first treated with a small quantity of nitric acid so long as red vapours are disengaged, then boiled with concentrated sulphuric acid till the gold has become compact, set aside to cool, diluted with water, and titrated as above.

#### Assaying on the Grain System.

It will be readily seen that the process just described may quite as conveniently be arranged on the grain system by substituting 10 grains of silver as the unit in place of the gramme, each decem of concentrated salt solution would then be equal to  $\frac{1}{10}$ th grain of silver, and each decem of decimal solution to  $\frac{1}{100}$ th grain.



## CYANOGEN.



1 CC or 1 dm.	$\frac{N}{10}$	silver solution	= 0.0052 Gm. or 0.052 grn.
			Cyanogen.
"	"	"	= 0.0054 Gm. or 0.054 grn.
			Hydrocyanic acid.
"	"	"	= 0.01302 Gm. or 0.1302 grn.
			Cyanide of potassium.
"	$\frac{N}{10}$	iodine	= 0.003255 Gm. or 0.03255 grn.
			Cyanide of potassium.

## 1. Liebig's Method.

§ 77. This ready and beautiful method of estimating cyanogen in prussic acid, alkaline cyanides, &c., was discovered by Liebig, and is fully described in the "Ann. der Chemie und Pharm.," vol. lxxvii, p. 102. It is based on the fact, that when a solution of nitrate of silver is added to an alkaline solution containing cyanogen, with constant stirring, no permanent precipitate of cyanide of silver occurs until all the cyanogen has combined with the alkali and the silver, to form a soluble double salt; (in the presence of potash, for example, KCy, AgCy.) If the slightest excess of silver, over and above the quantity required to form this combination, be added, a permanent precipitate of cyanide of silver occurs, the double compound being destroyed. If, therefore, the silver solution is of known strength, the quantity of cyanogen present is easily found; 1 eq. of silver in this case being equal to 2 eq. cyanogen.

So fast is this double combination that when chloride of sodium is present, no permanent precipitate of chloride of silver occurs until the quantity of silver necessary to form the compound is slightly overstepped.

In all cases the solution to be titrated must be rendered alkaline, if not already so. Essential oil of bitter almonds, or its spirituous solution, need generally the addition of a quantity of strong spirit to prevent turbidity, from the separation of the essential oil, which would otherwise interfere with the delicacy of the reaction.

When no alkali is present, it is still possible to titrate a solution containing cyanogen with silver, but in this case the precipitate of cyanide of silver appears at once, and double as much silver is required as when alkali is present. When the titration is conducted in this manner, the manipulations are precisely the same as with the determination of chlorine by silver, the silver solution being added, with constant shaking, until no further precipitate occurs. Liebig's method is however preferable.

Example with hydrocyanic acid: In order that each CC or dm. of  $\frac{N}{10}$  silver solution should represent 1 per cent. of anhydrous acid, it would be necessary to take 0.54 CC or dm. for the analysis, but this is too little to measure with accuracy, it is better to take ten times this quantity, = 5.4 CC or dm.; if the number of CC or dm. of silver solution required to produce the turbidity be divided by 10, or the decimal point moved one place to the left, the figures will represent the percentage of real prussic acid present.

5.4 CC, therefore, of the so called Scheele's hydrocyanic acid were carefully taken with a pipette, mixed with a small quantity of solution of potash, and titrated with  $\frac{N}{10}$  silver, of which 42.5 CC were required; the quantity of real acid contained in the sample was 4.25 %.

5.4 dm. of the *Acid. Hydrocy. dil. P. L.* were titrated as above and 19 dm.  $\frac{N}{10}$  silver required = 1.9 % real acid. The Pharmacopoeia orders the strength to be 2 per cent.

5.4 dm. *Aq. Lauro Cerasi* titrated as above required 9.5 dm., the strength was therefore 0.095%, the decimal point being removed two places to the left, as 100 times the quantity was taken.

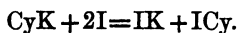
Caution.—In using the pipette for measuring hydrocyanic acid, it is advisable to insert a plug of cotton wool, slightly moistened with nitrate of silver, into the upper end, so as to avoid the danger of inhaling any of the acid, otherwise it is decidedly preferable to weigh it.

Example with cyanide of potassium: The quantity of this substance necessary to be taken for analysis, so that each CC or dm. shall be equal to 1 per cent. of the pure cyanide, is 1.30 Gm. or 13.0 grn. 13 grains, therefore, of the commercial article were dissolved in water, no further alkali being necessary, and 54 dm  $\frac{N}{10}$  silver required to produce the permanent turbidity, the sample therefore contained 54% of real cyanide.

The large quantities of this material used at the present time in electro-plating and photography render it frequently desirable to ascertain its chemical strength.

## 2. Method of Fordos and Gells.

This process, which is principally applicable to alkaline cyanides, depends on the fact that when a solution of iodine is added to one of cyanide of potassium the iodine loses its colour so long as any undecomposed cyanide remains. The reaction may be expressed by the following formula:—



Therefore, 2 at. iodine represent 1 at. cyanogen in combination; so that 1 CC of  $\frac{N}{10}$  iodine expresses the half of  $\frac{1}{10.000}$  at. cyanogen or its compounds. The end of the reaction is known by the yellow colour of the iodine solution becoming permanent.

Commercial cyanides are, however, generally contaminated with caustic or monocarbonated alkalies, which would equally destroy the colour of the iodine as the cyanide, consequently, these must be converted into bicarbonates, best done by adding carbonic acid water, (ordinary soda water.)

Example: 5 Gm. cyanide of potassium were weighed and dissolved in 500 CC water, then 10 CC (=0.1 Gm. cyanide) taken with a pipette, diluted with about  $\frac{1}{2}$  litre of water, an ounce or two of soda water added, then  $\frac{N}{10}$  iodine delivered from the burette until the solution possessed a slight but permanent yellow colour, 25.5 CC were required, which multiplied by 0.003255 gave 0.08300 Gm., instead of 0.1 Gm. or 83% real cyanide.

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**PHOSPHORIC ACID.  $PO_5=71$ .**

**1. By Precipitation as Phosphate of Uranium with Ferrocyanide of Potassium as Indicator.**

§ 78. THIS method is based on the fact that when nitrate or acetate of uranium is added to a solution of tribasic phosphoric acid containing acetate of ammonia and free acetic acid, the whole of the phosphoric acid is thrown down as double phosphate of uranium and ammonia, having a light lemon colour, and the composition  $2 (U_r, O_3), NH_4 O, PO_5 + Aq$ . When this precipitate is washed with hot water, dried and burned, the ammonia is entirely dissipated, leaving phosphate of uranium, which possesses the formula  $2 (U_r, O_3), PO_5$ , and contains in 100 parts 80.09 sesquioxide of uranium and 19.91 phosphoric acid. In the presence of fixed alkalies, instead of ammonia, the precipitate consists simply of phosphate of uranium. By this method phosphoric acid may be completely removed from all the alkalies and alkaline earths; also, with a slight modification, from iron; not, however, satisfactorily from alumina when present in any quantity.

The details of the process were fully described by me in the "Chemical News," February 4th, 1860, and immediately after the publication of that article, while employed in further in-

vestigation of the subject, I devised the volumetric method now to be described. Since that time it has come to my knowledge that Neubauer and Pincus had independently of each other and myself, arrived at the same process. This is not to be wondered at, if it be considered how easy the step is from the ordinary determination by weight to that of measure, when the delicate reaction between uranium and ferrocyanide of potassium is known. Moreover, the great want of a really good volumetric process for phosphoric acid in place of those hitherto used, has been felt by all who have anything to do with it, and consequently the most would be made of any new method possessing so great a claim to accuracy as the ordinary estimation of phosphoric acid by uranium undoubtedly does.

Neubauer appears to have been the earliest discoverer of the method. ("Archiv für wissenschaftliche Heilkunde," Bd. iv, p. 228.) The experiments of Pincus were announced in the "Journal für Prakt. Chem.," 76, 104, neither of which publications have I been able as yet to obtain. My own were not publicly described, inasmuch as the preparation of this book was in hand, and the process intended for insertion here.

The great advantages possessed by the method over Liebig's and Raewsky's iron process are that the combination between the phosphoric acid and uranium is definite and certain, and that the mixture needs no filtration, since phosphate of uranium produces no colour with ferrocyanide of potassium, like phosphate of iron. For the ready and accurate determination of phosphoric acid in manures and urine, the process is very serviceable.

#### Preparation of Standard Solutions.

Phosphate of Soda. 50.218 Gm. of pure crystallized phosphate of soda, freed from extraneous moisture by powdering and pressing between sheets of filtering paper, are dissolved in water, and the solution diluted to 1 litre; or 502.2 grains to

1000 dm. 1 CC or 1 dm. of the solution so obtained represents 0.01 Gm. or 0.1 grn. phosphoric acid.

**Solution of Uranium.** This is best made by dissolving crystals of nitrate of uranium in distilled water; the exact strength of the solution is then found by titrating a measured portion of the standard phosphate of soda with it as follows:— 50 CC of the latter are measured into a beaker, 3 or 4 CC of solution of ammonia added, then acetic acid in excess, and the mixture gently warmed; the beaker is then brought under a burette containing the uranium solution, and portions of it delivered in from time to time with constant stirring, until, when a drop taken out with a thin glass rod and placed in the middle of another larger drop of solution of yellow prussiate of potash (1 : 20) on a white plate, a faint but distinct chocolate brown colour is produced at the point of contact. A few moments should be allowed to elapse on the addition of each portion of uranium solution before testing, as the decomposition is not very rapid unless the fluid is considerably heated. Suppose that in this way the reaction has been produced with 29.5 CC of the uranium solution, that quantity is equivalent to 0.50 Gm.  $\text{PO}_5$ ; to save calculation, however, it is advisable to dilute it to the same strength as the phosphate of soda, which is done by measuring 295 CC, and adding distilled water to make up 500 CC or 590 CC to 1 litre. In case the point of saturation is overstepped in any analysis, a portion of the phosphate solution may be added, and the analysis corrected without loss of material. For most technical purposes the plan just described is sufficiently exact, but it must be borne in mind, that in order to produce the brown colour, a certain excess of uranium is necessary, and the excess required varies with the quantity of liquid; for it is manifest, that if the original uranium solution is titrated as above, so that the amount of fluid is about 4 oz., it would require a few drops less of the standard solution to produce the same shade of colour when the same quantity of phosphoric acid was contained in only 2 oz.

Consequently, when greater accuracy is required, the following plan should be adopted:—The uranium solution is contained in a burette graduated to  $\frac{1}{10}$  CC; 20 CC or thereabouts of the phosphate of soda are measured into a beaker, together with the requisite quantities of ammonia and acetic acid, the proportions of which, in any analysis, should always be as near as possible the same as used in the original titration; the rest of the manipulation is conducted as just described. When a sufficient quantity of the uranium has been added, to produce the distinct colour with a drop of ferrocyanide, the height of the total fluid in the beaker is marked by a slip of gummed paper, the contents emptied, and the glass again filled to the same height with water containing the same quantities of ammonia and acetic acid as were added to the phosphate, the uranium is then added, drop by drop, until a drop of the mixture produces the *same amount* of colour with ferrocyanide, as in the previous case; the quantity of uranium so required is deducted from that used for the phosphate, and thus the proportion found which was absolutely required to precipitate the phosphoric acid. If the same plan is pursued in all analyses, the greatest possible accuracy will be obtained however variable the amount of fluid.

Under most circumstances, however, the difference between the two methods is slight, unless the quantity of fluid varies considerably, but as the reaction of uranium with ferrocyanide is less sensitive in the presence of acetate of soda or ammonia than iron, the correction should be adopted where great accuracy is required. The process requires some amount of practice to ensure the best results, but when that is attained it is thoroughly reliable.

The following example is given as an evidence of the accuracy of results when no correction is made for the quantity of fluid:—

20 CC of the standard phosphate of soda were precipitated with the magnesia mixture for the estimation of phosphoric

acid, and yielded pyrophosphate of magnesia equal to 0.199 Gm.  $\text{PO}_5$ .

20 CC of the same phosphate solution were titrated with uranium solution, and required 10.7 CC to produce the faint brown colour; the mixture so prepared was diluted, boiled, and the precipitate washed by decantation through a filter, then collected, dried, and ignited, yielding 1.009 Gm.  $2(\text{U}_2\text{O}_5)\text{PO}_5 = 0.2009$  Gm.  $\text{PO}_5$ , instead of 0.199 Gm., or 100.7 instead of 100.

The process is applicable, volumetrically, to all phosphates of the first and second groups, but not to any of the so-called sesquioxides, having the formula  $\text{M}_2\text{O}_3$ , nor is it available in the presence of arsenic acid or any metals giving coloured precipitates with ferrocyanide of potassium, such as copper, &c.

The so-called superphosphates of lime and other manures containing soluble phosphoric acid are very readily examined by this method—since it is only necessary to lixiviate them at first with warm, and lastly with boiling, water, add ammonia to the liquid, then acetic acid in excess, and titrate at once. Iron or alumina, if present in the manure, will not be found, generally speaking, in the watery extract, or if so, only in very slight traces and will be left insoluble on the addition of the acetic acid. Should this be the case it is best to dilute the watery solution to a definite volume, allow the precipitate to settle thoroughly, and take an aliquot portion of the clear liquid for titration with uranium. When the watery solution is highly coloured with organic matter, it should be evaporated to dryness with a little nitric acid, then redissolved for titration.

Bones and bone-ash are dissolved in hydrochloric acid; the phosphates of lime and magnesia precipitated with ammonia, redissolved in acetic acid, then titrated as before.

Manures or other phosphoric acid compounds containing iron or alumina or both, are best dissolved in hydrochloric acid, and the whole of the phosphoric acid precipitated as a mixture of phosphates of lime, magnesia, iron, and alumina, by ammonia



in excess; the precipitate is brought upon a filter and the liquid drained away, the precipitate slightly washed, and when sufficiently drained it is treated two or three times with acetic acid on the filter, then washed, and the filtrate and washings containing all the phosphate of lime and magnesia collected and set aside. The residue on the filter, consisting of phosphate of iron and alumina, is dissolved on the filter with hydrochloric acid, the filter washed clean, and the acid filtrate and washings mixed with a tolerable quantity of tartaric acid, then a clear solution of ammonia, chloride of ammonium, and sulphate of magnesia added in excess to separate all the phosphoric acid as double phosphate of magnesia and ammonia; the solution should be allowed to stand 4 or 5 hours in a slightly warm place, the precipitate then collected in a filter, washed with ammoniacal water, then dissolved on a filter with acetic acid, and the solution so obtained mixed with the former liquid, and titrated with uranium as before described; the result gives the total amount of phosphoric acid present.

If lime only is present with the iron and alumina it is preferable to precipitate it first as oxalate, by adding oxalate and acetate of ammonia (the latter in good quantity) to the hydrochloric acid solution. The filtrate and washings are then treated with the tartarized magnesia solution to precipitate all the phosphoric acid.

**Magnesia Solution for Precipitating Phosphoric Acid.**

Crystallized sulphate of magnesia.....	1 part
Pure chloride of ammonium.....	1 "
Distilled water .....	8 parts
Solution of ammonia 10% ('96 spec. grav.)	4 "

After standing a few days filter for use.

**Tartarized Magnesia Solution for Precipitating Phosphoric  
Acid in the presence of Iron and Alumina.**

Crystallized sulphate of magnesia .....	12 parts
„ tartaric acid.....	15 „
Pure chloride of ammonium .....	16 „
Water .....	1000 „

Where the amounts of iron and alumina are very large in comparison with the phosphoric acid, it is better to adopt the method of separation originally proposed by Reynoso and afterwards modified by Girard, namely, as phosphate of tin.

To the solution of the substance in nitric acid pure granulated metallic tin is added, in the proportion of 5 or 6 parts to every part of phosphoric acid supposed to be present, and the mixture digested on the water bath for 2 or 3 hours, the fluid is then carefully decanted off through a filter, and repeatedly washed by decantation with hot water; yellow sulphide of ammonium is then added to the precipitate in the beaker to dissolve all the phosphate of tin, and whatever traces may have been retained on the filter are removed by eventually passing the sulphide solution through it; the insoluble compounds of alumina and iron are thus retained on the original filter, and washed with water containing sulphide of ammonium. Magnesia solution is then added to the clear greenish-yellow filtrate and washings, to precipitate all the phosphoric acid as double phosphate of magnesia and ammonia, which is collected, washed with ammoniacal water, dissolved in acetic acid, and titrated with uranium as before described.

It is of *great importance* that a sufficient quantity of acetate of ammonia, soda, or potash is always present in titrating with nitrate of uranium, lest any nitric acid should be set free and interfere with the accuracy of the results. On the other hand, a great excess interferes with the delicacy of reaction with ferrocyanide. The acetate of uranium may be used instead of

nitrate, but as its solution is decomposed to a certain extent by sunlight, or by empyreumatic matter in the acetic acid, the nitrate is preferable.

**Examples of analysis:** A sample of Gibbs' Peruvian guano was examined for soluble phosphoric acid, i.e., alkaline phosphates, and yielded pyrophosphate of magnesia equal to 2.5% phosphoric acid.

The same sample yielded 2.4% by the volumetric uranium process.

A sample of Peter Lawson and Sons' phospho-guano yielded 20.08% biphosphate of lime by the ordinary uranium process, and 20.1% by the volumetric. The first operation occupying 6 hours, the second, 10 minutes.

As uranium is somewhat costly it is well to collect the precipitates, where many analyses are made, in a large bottle, and when sufficient has been obtained, to recover the uranium for the same purpose by igniting the dry precipitate in a porcelain crucible, with the carbonaceous residue produced by burning tartrate of soda and potash in a covered crucible. By this means the uranium is reduced to protoxide, while the phosphoric acid unites with the potash and soda, and can be entirely extracted with boiling water; the insoluble protoxide is then dissolved in nitric acid and evaporated to dryness in the water-bath, redissolved in distilled water, and titrated in order to adjust its strength as before described.

## 2. By Precipitation as Phosphate of Lead, (Mohr.)

1 CC or 1 dm. $\frac{3}{10}$ nitrate of lead	=	0.0071 Gm. or 0.071 grn. $\text{PO}_5$
1 CC or 1 dm.       ,,       ,,	=	0.0155 Gm. or 0.155 grn. $\text{PO}_5 + 3 \text{CaO}$ .

This process devised by Mohr, and strongly recommended by him for the estimation of phosphoric acid in manures, &c., consists simply in adding the lead solution to the phosphates

until no further precipitate is produced. Unfortunately the separation of the precipitate is tardy and imperfect, so that the end of the reaction cannot be distinguished except by taking out a portion of the clear liquid for examination; to this end, however, the filtering tube of Dr. Beale, Fig. 15, is very serviceable; or if the precipitation takes place in a flask so as to permit of vigorous shaking, a better separation may be obtained, so that a little clear liquid may be poured from the surface into a test tube.

Another disadvantage is, that neither sulphuric nor hydrochloric acids may be present in the solution to be titrated, since insoluble lead compounds would be produced by both these acids; therefore acetic acid, or nitric acid with acetate of soda, can only be used as the solvents for the substance to be examined.

Phosphate of lead is insoluble in water and cold dilute acetic acid; it is, however, freely soluble in dilute mineral acids, and partially so in hot acetic acid. Therefore the titration must take place in cold, or only slightly warm liquids, (100 to 120° Fahr.)

Preparation of the Standard Solutions. Since 1 eq. phosphoric acid takes up 3 eq. of oxide of lead, it is necessary that the lead solution, in order to be decinormal as regards the phosphoric acid, should contain  $\frac{3}{10}$  eq. of lead. Therefore three times 16.557 Gm. = 49.671 Gm. of nitrate of lead are weighed and dissolved in 1 litre of distilled water, 496.71 grn. to 1000 dm. will give a solution of the same strength on the grain system.

A Decinormal Solution of Phosphate of Soda is required to titrate the lead solution or to correct an analysis. This is prepared by dissolving 35.8 Gm. of the pure salt in the litre, or 358 grains to the 1000 dm. This and the lead solution are then equal, volume for volume.

Examples: 1 Gm. dry and pure phosphate of lime was dissolved in a small quantity of nitric acid, then diluted, acetate of soda added, and 64.3 CC lead solution required to

precipitate all the  $\text{PO}_4$ .  $64.3 \times 0.0155 = 0.997$  Gm. phosphate of lime. A repetition gave 0.996 Gm.

The method is undoubtedly susceptible of good results, but requires extreme care and patience, and suffers under the great drawback of requiring the absence of sulphuric and hydrochloric acids; these can, however, readily be removed by baryta and silver, when necessary.

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### SUGAR.

§ 79. THE term sugar is applied to several bodies possessing distinct properties, and differing somewhat in chemical composition. There are only two classes, however, of general importance, that is to say:—

1. Those that possess the chemical composition of grape sugar or glucose,  $\text{C}_{12} \text{H}_{22} \text{O}_{11}$ , such as the sugar contained in the juice of grapes, apples, and other ripe fruit; also that which occurs in urine in *Diabetes mellitus*.

2. Common cane sugar,  $\text{C}_{12} \text{H}_{22} \text{O}_{11}$ , contained in the juice of the sugar cane, beet root, maple, &c.

Sugars of the latter class, and also those contained in milk, dextrine, &c., may all be converted into grape sugar by boiling with weak sulphuric acid, and must all be so converted before they can be estimated by the chemical method here given.

This method is based on the fact, that although a mixture of pure sulphate of copper, tartrate of potash, and caustic soda, mixed in proper proportions, may be boiled without undergoing change; yet, if only a trace of grape sugar be added, a very slight warming is enough to precipitate a portion of the copper as protoxide  $\text{Cu}_2 \text{O}$ .

Fehling, Neubauer, and others have very carefully examined the reaction which takes place, and found that 1 at. pure grape sugar = 180, is capable of reducing exactly 10 at. =

397 of oxide of copper ( $\text{Cu O}$ ) to the state of protoxide. Therefore, if the quantity of copper reduced by a given solution of sugar is known, it is easy to find the quantity of sugar present.

There are two methods of procedure—

1. To prepare a standard solution of pure sulphate of copper with tartrate of potash and caustic soda, and add the sugar solution to a definite quantity of it until the deep blue colour has disappeared; or—

2. To add the copper solution, which may be of indefinite strength, in excess, and estimate the precipitated protoxide, either by weight or indirectly, by the method of Schwarz, § 52, 2.

As the first method is susceptible of very accurate results and occupies little time, it is generally preferred. The requirements are as follows:—

Standard Solution of Copper. 34.64 Gm. of pure crystallized sulphate of copper, previously powdered and pressed between blotting paper, are weighed and dissolved in 200 CC of distilled water; in another vessel, 173 Gm. of pure crystals of double tartrate of soda and potash, (Rochelle salt,) are dissolved in 480 CC of solution of pure caustic soda, spec. grav. 1.14. The two solutions are then mixed, and the deep clear blue solution diluted with distilled water to 1 litre.

Each 10 CC of the solution so prepared, containing 0.3464 Gm. sulphate of copper, represent exactly 0.050 Gm. pure anhydrous grape sugar: the same solution may be prepared on the grain system, as in § 80, 10. It must be preserved in a dark place, and in well-stoppered bottles, kept tolerably full, since, if the solution absorbs much carbonic acid, a precipitate will occur in boiling even in the absence of sugar. This may, however, be prevented by adding fresh caustic alkali. In all cases before using it for titrating a solution of sugar, 10 CC should be boiled with about 40 CC of water, for a few minutes, in order to be certain of its fitness.

In order to obviate the difficulty connected with preserving the copper solution, Schiff ("Ann. d. Chem. u. Pharm.," 112,

p. 369) recommends the use of dry neutral tartrate of copper, prepared by precipitating 250 Gm. crystallized sulphate of copper in strong warm solution, with 280 Gm. Rochelle salt, also in warm solution. The light blue precipitate is drained on a filter, washed till pure, and dried by exposure to the air in a slightly warm room till it becomes thoroughly powdery. It then possesses the formula  $C_6H_4O_{10} + 2CuO + 6HO = 265.4$ , and contains 29.906% CuO; if dried at  $220^\circ$  in a current of air, it is anhydrous, and possesses the atomic weight 211.4, containing 37.58% CuO. 3.685 Gm. of the air dried, or 2.935 Gm. of the anhydrous salt, represent 0.5 Gm. pure grape sugar. When used for estimating sugar, either of these cupric tartrates may be used by mixing the necessary weighed quantity with sufficient caustic soda solution to produce a clear blue liquid.

However carefully the tartrate of copper is prepared, there is, I apprehend, never the same certainty respecting its composition as in the case of the sulphate; and owing to the fact that a certain quantity must be delicately weighed before use, many operators will prefer to pursue the general plan, which, after all, presents no difficulty with ordinary care and foresight.

#### The Solution of Sugar.

This must be so diluted as to contain  $\frac{1}{2}$  or at most 1% sugar; if on trial it is found to be stronger than this, it must be further diluted with a measured quantity of distilled water.

If the sugar solution to be examined is of dark colour, or likely to contain extractive matters which might interfere with the distinct ending of the reaction, it is advisable to heat a measured quantity to boiling, and add a few drops of milk of lime, allow the precipitate to settle, then filter through animal charcoal, and dilute with the washings to a definite volume.

From thick mucilaginous liquids, or those which contain a large proportion of albuminous or extractive matters, the sugar is best extracted by Prof. Graham's dialyzer.

Cane, beet, and maple sugar juice, or prepared sugars, are converted into grape sugar by heating 30 or 40 CC of the clarified liquid in a water bath, with 30 or 40 drops of dilute sulphuric acid, (1 to 5,) for an hour or two, replacing the evaporated water from time to time; the acid is then neutralized with carbonate of soda, and the liquid diluted to 15 or 20 times its volume before being titrated.

100 parts grape sugar so found represent 95 parts cane sugar, or 10 CC copper solution are reduced by 0.0475 Gm. cane sugar. Starch or dextrine, or substances containing them, require to be heated longer with the acid in order to insure their conversion into glucose. To convert 1 Gm. starch into dextrine and thence into sugar, it should be mixed with 10 CC cold water, smoothly, then heated gently until thick, then add 12 drops dilute acid as before, and boil in a small flask, supported obliquely on a sand-bath, for 8 or 10 hours, replacing the water from time to time, then neutralize and dilute as before.

The change may be produced more rapidly and at lower temperature by using some form of diastase in place of sulphuric acid; an infusion of malt is best suited to the purpose, but the temperature must not exceed 160° Fahr., (71° C.); about four hours' digestion is sufficient. A like quantity of the same malt solution must be digested alone, at the same temperature, and titrated for its amount of sugar, which is deducted from the total quantity found in the mixture.

100 parts of grape sugar so found represent 90 parts of starch, ( $C_{12}H_{10}O_{10}$ ) or 10 CC copper solution, are reduced by 0.45 Gm. starch.

Sugar of milk may also be converted into grape sugar by boiling for a short time with dilute sulphuric acid, for although it possesses the same ultimate composition as grape sugar, it has of itself a special and somewhat uncertain action upon the copper solution, therefore it must be converted into grape sugar before being estimated.



**The Analytical Process.**

10 CC of the copper solution are measured into a convenient-sized flask or a white porcelain dish, and diluted with 40 CC of water, or, if necessary, the same quantity of dilute caustic soda, and brought to gentle boiling. The dilute sugar solution is then delivered in from time to time from a graduated burette or pipette; when the precipitated oxide of copper appears of a bright red colour, the lamp should be removed and the precipitate allowed to settle; if the flask is then held before a window, or the dish lifted on one side so as to cause the clear liquid to flow against the white porcelain, the colour may readily be seen; should any blue tinge remain more sugar solution is added, and the boiling recommenced and continued until all colour just disappears. If any doubt exists, a small portion of the *hot* mixture should be filtered, acidified with acetic acid, and a drop of solution of ferrocyanide of potassium added; if copper is in excess, a brown colour or precipitate will be produced.

It is almost impossible to hit the exact point on the first trial, but it affords a very good guide for a more exact titration the second time; the quantity of sugar solution necessary to discharge the colour from 10 CC copper solution contains 0.05 Gm. grape sugar.

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## PART V.

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### SPECIAL APPLICATIONS OF THE VOLUMETRIC SYSTEM TO COMPLETE QUANTITATIVE ANALYSIS.

#### ANALYSIS OF URINE.

§ 80. THE complete and accurate determination of the normal and abnormal constituents of urine presents more than ordinary difficulty to even experienced chemists, and is a hopeless task in the hands of any other than such. Fortunately however the most important matters, such as urea, uric acid, phosphates, sulphates, and chlorides, can all be determined volumetrically with accuracy by ordinary operators, or by medical men who cannot devote much time to practical chemistry. The researches of Liebig, Neubauer, Bence Jones, Vogel, Beale, Hassall, and others, during the last few years, have resulted in a truer knowledge of this important secretion, and to the two first mentioned chemists we are mainly indebted for the simplest and most reliable methods of estimating its constituents. With the relation which the proportion of these constituents bear to health or disease, the present treatise has nothing to do, its aim being simply to point out the readiest and most reliable methods of determining them quantitatively. Their pathological importance is very fully treated by some of the authorities just mentioned, among the

works of which Neubauer and Vogel's "Analyse des Harns," (said to be in process of translation by the New Cavendish Society,) and Prof. Lionel Beale's "Urine, Urinary Deposits, and Calculi," are most prominent and exhaustive.

The grain system of weights and measures will be adopted throughout this section, as being more readily applicable by medical men, while those who desire to use the gramme system will have no difficulty in working, when once the simple relation between them is understood, see § 6. The question of weights and measures is, however, of very little consequence, if the analyst considers that he is dealing with relative parts or proportions only, and as urine is generally described as containing so many parts of urea, chlorides, or phosphates, per 1000, the absolute weight may be left out of the question. The grain system, however, is more readily calculated into English ounces and pints, and therefore is generally more familiar to the medical profession of this country.

One thing, however, is necessary as a preliminary to the examination of urine, and which has not generally been sufficiently considered, that is to say, the relation between the quantity of secretion passed in a given time, and the amount of solid matters found in it by analysis. In a medical point of view, it is a mere waste of time, generally speaking, to estimate the constituents in half a pint or so of urine, passed at any particular hour of the day or night, without ascertaining the relation which that quantity, with its constituents, bears to the whole quantity passed during, say 24 hours; and this is the more necessary, as the amount of fluid secreted varies very considerably in healthy persons; beside this, the analyst should register the colour, peculiarity of smell, if any, consistence, presence or absence of a deposit, (if the former, it should be collected for separate analysis, filtered urine only being used in such cases for examination,) and lastly its reaction to litmus should be observed.

## 1. Specific Gravity.

This is best taken by measuring 100 dm. into an accurately tared beaker or flask, the increase of weight in grains will be the spec. grav., water being 1000. 50 or 25 dm. may be taken instead of 100, in which case the weight multiplied by 2 or 4 will be the spec. grav. Where an accurate balance or weights are not at hand, a good urinometer may be used.

## 2. Estimation of Chlorides, (calculated as Chloride of Sodium.)

This may be done in two ways, viz. :—

a. By Nitrate of Silver, (Mohr.) 10 dm. of the urine are measured into a thin porcelain or platinum capsule, and 15 grains of nitrate of potash in powder added; the whole is then evaporated to dryness, and gradually heated till the residue becomes white; it is then dissolved in a small quantity of water, and the carbonate of potash, produced by the combustion of the organic matter, *nearly* neutralized by dilute nitric acid; two or three drops of solution of chromate of potash are then added, and the mixture titrated with  $\frac{N}{10}$  silver as in § 74. Each dm. of silver solution represents 0.05846 grn. salt, consequently if 12.5 dm. have been used, the weight of salt in the 10 dm. of urine is 0.73075 grn., and as 10 dm. only was taken, the weight multiplied by 10, or what amounts to the same thing, the decimal point moved one place to the right, gives 7.3075 grains of salt for 1000 of urine.

In order to save calculation, it is convenient to measure 5.9 dm. of the urine, add about 10 grains of nitrate of potash, then evaporate, ignite, and titrate as before directed; the number of decems of  $\frac{N}{10}$  silver used will represent the number of grains of salt in 1000 grains of urine.

Example: 5.9 dm. of urine passed by a patient suffering from *Diabetes insipidus* was evaporated and titrated as above, re-

quiring 3.1 dm. silver solution, the proportion of salt was therefore 3.1 grn. per 1000 of urine.

Where the quantity of chlorides is small, it may be advisable to use larger quantities of urine, say 58.5 dm.; in that case one-tenth of the number of dm. of silver solution required will be the number of grains of salt per 1000 urine.

b. By Nitrate of Mercury, (Liebig.) The principle of this method is as follows:—If a solution of nitrate of mercury, free from any excess of acid, is added to a solution of urea, a white gelatinous precipitate is produced, containing urea and oxide of mercury in the proportion of 1 eq. of the former to 4 eq. of the latter, ( $4 \text{ Hg O} + \text{Ur.}$ ) When chloride of sodium, however, is present in the solution, this precipitate does not occur, until all the chloride of sodium is converted by double decomposition into chloride of mercury (sublimite) and nitrate of soda, the solution remaining clear; if the exact point be overstepped, the excess of mercury immediately produces the precipitate above described, so that the urea present acts as an indicator of the end of the process. It is therefore very easy to ascertain the proportion of chlorides in any given sample of urine by this method, if the strength of the mercurial solution is known; since 1 eq. of oxide of mercury converts 1 eq. of chloride of sodium into 1 eq. each of corrosive sublimate and nitrate of soda. The strength of the standard solution of nitrate of mercury is best arranged as follows:—

1. Standard Solution of Nitrate of Mercury. It is of great importance that the solution be pure, for if the mercury from which it is made be contaminated with traces of other metals, such as bismuth, silver, or lead, they will produce a cloudiness in the liquid while under titration, which may possibly hinder the exact ending of the reaction; therefore 184.2 grn. of the purest red oxide of mercury, or 170.6 grn. of pure metallic mercury (the former is preferable, as being easier to weigh and less likely to be impure) are put into a beaker, with

a sufficiency of pure nitric acid of about 1.20 spec. grav. to dissolve them by the aid of a gentle heat, the clear solution so obtained is evaporated on the water bath to remove any excess of free acid. When the liquid is dense and syrupy in consistence, it may be transferred to the graduated cylinder or flask and diluted to 1000 dm. (10,000 grains,) 1 dm. of the solution so prepared is equal to 0.1 gm. chloride of sodium, or 0.06065 gm. chlorine. If on diluting the concentrated mercurial solution a yellow precipitate of basic nitrate of mercury should form, it must be allowed to settle, the clear liquid poured off, and a few drops of nitric acid added to the precipitate to redissolve it; the whole is then mixed and preserved for future use in a well-stoppered bottle. It is always preferable to have this precipitate formed on dilution, as it is a proof of there being no excess of acid, which would considerably interfere with the accuracy of results.

2. The Baryta Solution. Before urine can be submitted to titration by the mercurial solution, it is necessary to remove the phosphoric acid, and the proper agent for this purpose is a mixture composed of 1 volume of cold saturated solution of pure nitrate of baryta and 2 volumes ditto caustic baryta; the same agent is used previous to the estimation of urea, and may be simply designated "Baryta Solution."

3. The Analytical Process. 40 dm. of the clear urine are mixed with 20 dm. of baryta solution, and the thick mixture poured upon a small dry filter; when sufficient clear liquid has passed through, 15 dm.=10 dm. urine, are taken with a pipette and just neutralized, if necessary, with a drop or two of nitric acid; if not alkaline, the probability is that sufficient baryta solution has not been added to precipitate all the phosphoric and sulphuric acids; this may be known by adding a drop or so of the baryta solution to the filtrate; if any precipitate is produced, it will be necessary to mix off a fresh quantity of urine with three-fourths or an equal quantity of baryta, in which case  $17\frac{1}{2}$ , or 20 dm. must be taken to represent

10 dm. of the urine; the excess in either case of baryta must be cautiously neutralized with nitric acid.

The vessel containing the fluid is then brought under a Mohr's burette containing the mercurial solution, and small portions delivered in with stirring, until a distinct permanent precipitate is produced; it may happen that a turbidity is produced from the very first drop or two, owing to slight impurities in the mercurial solution, but as this will not increase, the point when the urea precipitate appears is not difficult to determine; the volume of solution used is then read off and calculated for 1000 parts of urine.

Example: 15 dm. of the liquid prepared with a sample of urine, as in 3 (=10 dm. urine) required 6.2 dm. mercurial solution, the quantity of salt present was therefore 0.62 grn., or 6.2 grn. in 1000 grains of urine.

### 3. Estimation of Urea, (Liebig.)

The combination between urea and oxide of mercury in neutral or alkaline solutions has been alluded to in the foregoing article on chlorides; it will therefore probably be only necessary to say that the determination of urea in urine is based on that reaction; and as the precipitate so produced is insoluble in water or weak alkaline solutions, it is only necessary to prepare a standard solution of mercury of convenient strength, and to find an indicator by which to detect the point when all the urea has entered into combination with the mercury, and the latter slightly predominates. This indicator is carbonate of soda. If, in the course of adding the mercurial solution from the burette to the urine, a drop of the mixture be taken from time to time and brought in contact with a few drops of solution of carbonate of soda on a glass plate, slab, or watch glass, no change of colour is produced at the point of contact until the free urea is all removed; when this is the case, and the nitrate of mercury is slightly in excess, a yellow colour is produced, owing to the formation of hydrated oxide of mercury.

The compound of urea and mercury consists, according to Liebig's analysis, of 1 eq. of the former to 4 of the latter, that is to say, if the nitric acid set free by the mixture is neutralized from time to time with carbonate of soda or other suitable alkali. If this be not done, the precipitate first formed alters in character, and eventually consists only of 3 eq. of mercury with 1 of urea. In order to produce the yellow colour with carbonate of soda, there must be an excess of mercurial solution; theoretically, 100 parts of urea should require 720 parts of oxide of mercury; but practically, 772 parts of the latter are necessary to remove all the urea, and at the same time show the yellow colour with alkali, consequently the solution of nitrate of mercury must be of empirical strength, in order to give reliable results.

**Preparation of the Standard Solution.** 772 grains of red oxide of mercury, or 715 grains of the metal itself, are treated with nitric acid, as described in the article on chlorides, 2, b 1, and in either case diluted to 1000 dm., (10,000 grains,) 1 dm. of the solution is then equal to 0.1 grn. urea. (The extreme care required to remove traces of foreign metals from the mercury is not so necessary here as in the foregoing instance.)

**2. The Analytical Process.** Two volumes of the urine are mixed with one of baryta solution, as before described in 2, b 3, of this section (reserving the precipitate for the determination of phosphoric acid, if necessary,) and 15 dm. = 10 dm. urine, taken in a small beaker for titration; it is brought under the burette containing the mercurial solution, (without neutralizing the excess of baryta, as in the case of chlorides,) and the solution added in small quantities so long as a distinct precipitate is seen to form, a plate of glass laid over dark paper is previously sprinkled with a few drops of solution of carbonate of soda, and a drop of the mixture must be brought from time to time, by means of a small glass rod, in contact with the soda; so long as the colour remains white, free urea is present in the mixture; when the



yellow colour is distinctly apparent, the addition of mercury is discontinued, and the quantity used calculated for the amount of urea. It is always advisable to repeat the analysis, taking the first titration as a guide for a more accurate estimation by the second.

Example: 15 dm. of urine deprived of phosphates=10 dm. of the original urine was titrated as described, and required 17·6 dm. of mercurial solution; consequently there was 1·76 grn. urea present in the 10 dm., or 17·6 grains in the 1000 of urine.

3. Corrections and Modifications. In certain cases the results obtained by the above method are not strictly correct, owing to the variable state of dilution of the liquids. The errors are, however, generally so slight as not to need correction. Without entering into a full description of their origin, I shall simply record the facts, and give the modifications necessary to be made where thought desirable.

a. The Urine contains more than 2 per cent. of Urea, i.e., more than 20 grains per 1000. This quantity of urea would necessitate 20 dm. of mercurial solution for 10 dm. of urine; all that is necessary to be done when the first titration has shown that over 2% is present, is to add half as much water to the urine in the second titration as has been needed of the mercurial solution above 20 dm. Suppose that 28 dm. have been used at first, the excess is 8 dm., therefore 4 dm. of water is added to the fluid before the second experiment is made.

b. The Urine contains less than 2% of Urea. In this case, for every 4 dm. of mercurial solution less than 20, 0·1 dm. must be deducted, before calculating the quantity of urea; so that if 16 dm. have been required to produce the yellow colour with 10 dm. urine, 15·9 is to be considered the correct quantity.

c. The Urine contains more than 1% of Chloride of Sodium, i.e., more than 10 grs. per 1000. In this case 2 dm.

must be deducted from the quantity of mercurial solution actually required to produce the yellow colour, with 10 dm. urine.

d. The Urine contains Albumen. In this case 50 dm. of the urine are boiled with 2 drops of strong acetic acid to coagulate the albumen, the precipitate allowed to settle thoroughly, and 30 dm. of the clear liquid mixed with 15 dm. baryta solution, filtered, and titrated for both chlorides and urea, as previously described.

e. The Urine contains Carbonate of Ammonia. The presence of this substance is brought about by the decomposition of urea, and it may sometimes be of interest to know the quantity thus produced, so as to calculate it into urea.

As its presence interferes with the correct estimation of urea direct, by mercurial solution, a portion of the urine is precipitated with baryta as usual, and a quantity, representing 10 dm. urine, evaporated to dryness in the water-bath to expel the ammonia, the residue then dissolved in a little water, and the urea estimated in the ordinary way. On the other hand, 50 or 100 dm. of the urine, not precipitated with baryta, is titrated with normal sulphuric acid and litmus paper, (see 9,) each dm. of acid representing 0.17 grn. ammonia, or 0.30 grn. urea.

#### Titration of the Mercurial Solutions.

Properly speaking, no standard solutions should be used for analysis without being first titrated to ascertain their exact chemical power and to guard against accidental errors. However pure the substances from which they are made may be thought to be, it sometimes occurs that the solutions do not strictly bear the proper strength: it may also happen that absolutely pure materials are not at hand, in which case ordinary kinds may sometimes be used, if the solutions made from them be tested by experiment. In the present case, should neither pure mercury or its oxide be obtainable, the commercial

metal may be dissolved in nitric acid, the solution boiled to expel all excess of the latter, then set aside that crystals of protonitrate of mercury may form, these are carefully separated from the mother liquor by draining in a funnel lightly stuffed with cotton wool, washed with cold water, then dissolved in a small quantity of dilute nitric acid, diluted to a certain extent with water, and a measured portion titrated for the quantity of mercury by the following process devised by Liebig, which is also applicable to the estimation of peroxide of mercury for some other purposes.

The principle of the process depends on the fact that phosphate of soda precipitates phosphate of mercury from a solution of pernitrate, but not from perchloride of that metal, if, therefore, the solution containing the precipitate of phosphate of mercury produced in the first case, be treated with a solution of chloride of sodium, the precipitate will disappear, from the circumstance that perchloride of mercury (sublimite) and phosphate of soda are formed, which both remain in solution. Consequently, if the strength of the solution of salt is known, the quantity of mercury is easily found, since 1 eq. of salt represents 1 eq. of oxide of mercury, (in the form of phosphate.) It is necessary, however, that directly the mercury is precipitated by the phosphate of soda, the chloride of sodium be added, otherwise the precipitate of phosphate becomes crystalline, and is not so readily decomposed by the salt.

The salt solution may conveniently be decinormal, § 74, containing 58.46 grn. to 100 dm.—each dm. represents 0.108 grn. HgO.

The solution of phosphate of soda is simply saturated at ordinary temperature.

Process: 10 dm. of the mercurial solution, not too concentrated, are measured into a beaker; 4 dm. of the phosphate of soda solution added, and the mixture *immediately* brought under the burette containing the solution of salt, which is added carefully, with constant stirring, until the precipitate

just disappears. Suppose that 18.2 dm. have been required, that number multiplied by 0.108 will give 1.9656 grn. HgO in the 10 dm. of solution; but the mercurial solution for determination of chlorides requires 1.842 grn. in the 10 dm.; therefore, by a rule-of-three calculation, 9.3 dm. of this particular solution must be diluted to 10 dm. with water, to be of the proper strength, or 930 dm. to 1000 dm.

The results so obtained are not, however, strictly correct, owing to the fact that a slight excess of salt is always necessary to redissolve the precipitate. If the process be reversed, the same objection applies, since an excess of mercury is necessary to produce a permanent precipitate.

The exact point, however, is reached by combining the two methods. For instance:—

Method 1. 10 dm. of mercurial solution with 4 dm. of phosphate of soda are titrated with salt solution and require 12.5 dm.

Method 2. 12.5 dm. of the same salt solution, as in 1, are measured; 4 dm. phosphate of soda added, and titrated with the mercurial solution, of which 10.25 dm. shall be required.

The following calculation will give the true power of the solutions—

1. 10 dm. mercury	=	12.5 dm. salt
2. 10.25 dm. „	=	12.5 „
<hr/>		<hr/>
20.25 dm. „ therefore	=	25.0 „

As the strength of the salt solution is known, the quantity of mercury contained in the 20.25 dm. is readily ascertained by a little calculation.

#### 4. Estimation of Sulphuric Acid.

100 dm. of the urine are measured into a beaker heated to boiling on a sand bath, or suspended in a retort ring over a spirit lamp, and the amount of sulphuric acid determined direct with normal chloride of barium, as in § 28, 3, using Beale's

filter for ascertaining the end of precipitation ; or, a special solution of chloride of barium may be prepared by dissolving 305 grains of the pure salt in 1000 dm. of water, 1 dm. of the solution is then equal to 0.1 grn.  $\text{SO}_4$  ; the manipulation in either case is the same as in § 28.

### 5. Estimation of Phosphoric Acid.

Hitherto the estimation of this substance volumetrically presented peculiar difficulties, but the discovery of the uranium process, § 78, 1, has set these entirely aside, so far as urine and many other bodies are concerned. The standard solution of nitrate of uranium is the same as described in § 78, 1, of which 1 dm. represents 0.1 grn. phosphoric acid, and the process of titration the same as there described.

50 dm. of the clear filtered urine are measured into a small beaker, 3 or 4 dm. of solution of ammonia, about 0.96 spec. grav., added, and the precipitate redissolved with an excess of acetic acid ; the mixture is then warmed in the water bath, or otherwise, and the uranium solution delivered in from the burette, with constant stirring, as long as a precipitate is seen to occur ; a small drop of the mixture is then removed with a thin glass rod, and placed in the middle of a drop of ferrocyanide of potassium solution, (1 : 20,) several large drops of which have been previously placed upon a white porcelain slab or plate ; so long as no brown colour is produced, the addition of uranium may be continued ; when the faintest indication of this reaction is seen, the process must be stopped, and the amount of colour observed ; if it coincides with the original titration of the uranium solution with similar quantities of water, acetate of ammonia, and acetic acid, the result is satisfactory, and the quantity of solution used may be calculated for the total phosphoric acid contained in the 50 dm. of urine ; if the uranium has been used accidentally in too great quantity, 10 or 20 dm. of the same urine may be added, and the titration concluded more

cautiously. Suppose, for example, that the solution has been added in the right proportion, and 9·6 dm used, the 50 dm. will have contained 0·96 grn. phosphoric acid. With care and some little practice the results are very satisfactory.

A rather more exact method of procedure is as follows :—

The precipitate produced by the baryta solution in 50 dm., or any other convenient quantity of urine, § 80, 2, 3, after the fluid is filtered from it, is washed once with cold water, and treated while still on the filter with warm acetic acid, to dissolve all the phosphate of baryta, which passes through the filter leaving the sulphate behind ; the filter is then washed with a small quantity of boiling water, to remove the last traces of phosphate ; sufficient ammonia is added to the solution, to neutralize the acetic acid, unless the quantity of the latter be large, when somewhat less than enough to neutralize may be added ; under any circumstances the liquid must be freely acidified with acetic acid before being titrated, and must contain a tolerable quantity of acetate of ammonia. Where great accuracy is not required, it will not be necessary to make any correction for the slight excess of uranium required to produce the brown colour with yellow prussiate of potash, as described in § 78, 1, otherwise the titration is precisely the same as there described ; 1 dm. of uranium solution precipitates 0·1 grn.  $\text{PO}_5$ .

A somewhat shorter and less troublesome method is to make a hole in the filter containing the mixed phosphate and sulphate of baryta, wash the whole precipitate with a small quantity of boiling water into a small beaker, then pour acetic acid on the filter, so as to remove all soluble matter, and add enough acetic acid to the fluid to dissolve all the phosphate ; add 3 or 4 dm. of ammonia, and if necessary, acetic acid in excess, then titrate with the uranium solution at once ; the precipitate of sulphate of baryta does not interfere with the reaction in the slightest.

In examining urinary sediment or calculi for phosphates, it is simply necessary to digest them with acetic acid, wash on a filter

with hot water, then titrate the solution and washings with uranium as above.

**Earthy Phosphates.** The above determination gives the total amount of phosphoric acid, but it may sometimes be of interest to know how much of it is combined with lime and magnesia. To this end 100 or 200 dm. of the urine are measured into a beaker, and rendered freely alkaline with ammonia; the vessel is then set aside for ten or twelve hours, for the precipitate of earthy phosphates to settle; the clear fluid is then decanted through a filter, the precipitate brought upon it and washed with ammoniacal water; a hole is then made in the filter and the precipitate washed through, the paper moistened with a little acetic acid, and washed into the vessel containing the precipitate, which latter is dissolved in acetic acid, some acetate of ammonia added, and the mixture titrated as before described; the quantity of phosphoric acid so found is deducted from the total previously estimated, and the remainder gives the quantity existing in combination with alkalies.

#### 6. Estimation of Uric Acid.

The determination of uric acid in urine is not often considered of much consequence, there are, however, circumstances under which it is desirable, especially in urinary deposits. As the quantity present in urine is very small it is necessary to take say from 300 to 500 dm. for the estimation.

The urine being measured into a beaker, from 5 to 8 dm. of pure hydrochloric acid are added, the whole well mixed, covered with a glass plate, and set aside in a cool place for 24 or 30 hours; at the end of that time the uric acid will be precipitated, in small crystals, upon the bottom and sides of the beaker, the supernatant liquid is decanted, washed once with cold distilled water, then dissolved in a small quantity of pure solution of potash, diluted to 6 or 8 ounces with distilled

water, acidified strongly with sulphuric acid, and titrated precisely as oxalic acid, § 43, 3, with  $\frac{N}{10}$  permanganate, each dm. of which is equal to 0.075 grn. uric acid. This method is not absolutely correct, owing to the fact that with the uric acid there is always precipitated a certain amount of colouring matter of the urine which destroys the permanganate equally with the uric acid. The method by weighing is, however, open to the same objection, beside being very troublesome, so that no advantage is gained by the latter plan.

#### 7. Estimation of Lime and Magnesia.

100 dm. of the urine are precipitated with ammonia, the precipitate redissolved in acetic acid, and sufficient oxalate of ammonia added to precipitate all the lime present as oxalate; the precipitate is allowed to settle in a warm place, then the clear liquid passed through a small filter, the precipitate brought upon it, washed with hot water, the filtrate and washings set aside, then the precipitate, together with the filter, pushed through the funnel into a flask, some sulphuric acid added, the liquid freely diluted, and titrated with permanganate of potash precisely as in §§ 43, 3; 60, 1; each dm. of  $\frac{N}{10}$  permanganate required represents 0.028 grn. lime.

Instead of the above method the following may be adopted:—

The precipitate of oxalate of lime after being washed is dried and, together with the filter, ignited in a platinum or porcelain crucible, by which means it is converted into a mixture of caustic and carbonate of lime. It is then transferred to a flask by the aid of the washing bottle, and an excess of normal nitric acid delivered in with a pipette; the amount of acid over and above what is required to saturate the lime, is found, by normal caustic alkali, precisely as described in § 18; each dm. of normal acid being equal to 0.28 grn. lime.

In examining urinary sediment or calculi for oxalate of lime,



it is first treated with caustic potash to remove uric acid and organic matter, then dissolved in sulphuric acid, freely diluted, and titrated with permanganate, as in § 60, 1; each dm.  $\frac{N}{10}$  permanganate represents 0.064 grn. oxalate of lime.

**Magnesia.** The filtrate and washings from the precipitate of oxalate of lime are then made alkaline with ammonia, and set aside for 8 or 10 hours in a slightly warm place, that the magnesia may separate as double phosphate of magnesia and ammonia, the supernatant liquid is then passed through a small filter, the precipitate brought upon it, washed with ammoniacal water in the cold, and dissolved in acetic acid, then titrated with uranium solution, as in §§ 38, 78, 1; each dm. of solution required represents 0.0563 grn. magnesia.

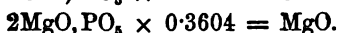
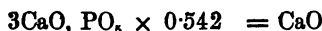
**Indirect estimation of the Lime and Magnesia existing as Phosphates.** Two portions of the urine, each measuring 200 dm., are put into beakers and precipitated with ammonia in excess, as in the case of estimating earthy phosphates, § 80, 5. In the one case the precipitate is collected, washed, dried, ignited, and weighed, the weight being noted.

The precipitate from the other 200 dm. of urine, is collected, washed, and dissolved in acetic acid, and titrated for phosphoric acid with uranium.

The calculation is then as follows:—

The weight of phosphoric acid is multiplied by the factor 2.1831, and from the number so obtained is deducted the weight of the total earthy phosphates estimated as above. If the remainder be multiplied by 2.5227, the weight of phosphate of magnesia will be obtained, and by difference also the phosphate of lime.

The amounts of lime and magnesia are obtained as follows:—



The principle is the same as in the estimation of the mixed alkaline chlorides, § 75, *h*.

## 8. Ammonia.

The only method hitherto applied to the determination of ammonia in urine, is that of Schlösing, which consists in placing a measured quantity of the urine, to which milk of lime is previously added, under an air-tight bell-glass, together with an open vessel containing a measured quantity of titrated acid. In the course of from 24 to 36 hours, all the ammonia will have passed out of the urine into the acid, which is then titrated with standard alkali to find the amount of ammonia absorbed.

One great objection to this method is the length of time required, since no heating must be allowed, urea being decomposed into free ammonia, when heated with alkali; there is also the uncertainty as to the completion of the process, and if the vessel be opened before the absorption is perfect, the analysis is spoiled. The following plan is recommended as in most cases suitable. When a solution containing salts of ammonia is mixed with a measured quantity of free fixed alkali of known strength, and boiled until ammoniacal gas ceases to be evolved, it is found that the resulting liquid has lost so much of the free alkali as corresponds to the ammonia evolved, § 16; that is to say, the acid which existed in combination with the ammonia in the original liquid has simply changed places, taking so much of the fixed alkali (potash or soda) as is equivalent to the ammonia it has left to go free. In the case of urine being treated in this way, the urea will also be decomposed into free ammonia, but happily in such a way as not to interfere with the estimation of the original amount of ammoniacal salts. The decomposition is such that while free ammonia is evolved from the splitting up of the urea, carbonate of fixed alkali (say potash) is formed in the boiling liquid, and as this reacts equally as alkaline as though it were free potash, it does not interfere in the slightest degree with the estimation of the original ammonia.

The following is the best method of procedure :—

100 dm. of the urine are exactly neutralized with normal alkali, as in the following article, No. 9, for the estimation of free acid ; it is then put into a flask capable of holding five or six times the quantity ; 10 dm. of normal alkali added, and the whole brought to boiling, taking care that the bladders of froth which at first form do not boil over ; after a few minutes these subside, and the boiling proceeds quietly ; when all ammoniacal fumes are dissipated, the lamp is removed, and the flask allowed to cool slightly ; the contents then emptied into a tall beaker, and normal nitric acid delivered in from the burette with constant stirring, until a fine glass rod or small feather dipped in the mixture and brought in contact with neutral or violet coloured litmus paper produces neither a blue nor red spot ; the number of dm. of normal acid are deducted from the 10 dm. of alkali, and the rest calculated as ammonia. 1 dm. alkali = 0.17 grn. ammonia.

Example : 100 dm. of urine were taken, as in 9, and required 0.7 dm. normal alkali to saturate its free acid ; 10 dm. alkali were then added, and the mixture boiled until a piece of moistened red litmus paper was not turned blue when held in the steam ; 4.5 dm. of normal acid were afterward required to saturate the free alkali ; the quantity of ammonia was therefore equal to 5.5 dm., which multiplied by 0.17 gave 0.935 grn. in 1000 of urine.

It must be borne in mind that the plan just described is not applicable to urine which has already suffered decomposition by age or other circumstances so as to contain carbonate of ammonia ; in this case it would be preferable to adopt Schlösing's method ; or where no other free alkali is present, direct titration with normal acid may be adopted.

### 9. Estimation of Free Acid.

The acidity of urine is doubtless owing to variable substances, among the most prominent of which appear to be acid phos-

phate of soda and lactic acid, other free organic acids are probably in many cases present; under these circumstances, the degree of acidity cannot be placed to the account of any particular body; nevertheless it is frequently desirable to ascertain its amount, which is best done as follows:—

100 dm. of the urine is measured into a beaker, and normal alkali, § 11, delivered in drop by drop from a small burette, until a thin glass rod or feather, moistened with the mixture and streaked across some well-prepared violet litmus paper produces no change of colour; the degree of acidity is then registered as being equal to the quantity of normal alkali used.

#### 10. Estimation of Diabetic Sugar.

The principle of the process is explained in § 79, and the copper solution required is precisely the same as there described, that is to say, 346·4 grains of pure sulphate of copper are dissolved in about 200 dm. of water. In another vessel 1730 grains of pure crystallized tartrate of soda and potash (Rochelle salt) are dissolved in 480 dm. of solution of pure caustic soda, spec. grav. 1·14. The two solutions are then mixed, well agitated, and diluted to 1000 dm. 1 dm. of the solution so prepared represents 0·05 grn. grape or diabetic sugar. It must be preserved in the dark, and in well-stoppered full bottles. It should bear heating when diluted with about four or five times its quantity of distilled water, without any precipitate taking place, and should always be submitted to this test before being used; if any does occur, it probably arises from the alkali having absorbed carbonic acid; in this case the addition of a little fresh caustic soda solution remedies the evil.

The Analytical Process. 10 dm. of the clear urine are diluted by means of a measuring flask to 200 dm. with water, and a large burette filled with the fluid; 10 dm. of the copper solution ( $=\frac{1}{2}$  grn. sugar) are then measured into a flask or white

porcelain capsule, 40 dm. of distilled water added, the vessel arranged over a spirit lamp under the burette, and brought to boiling, the diluted urine is then delivered in cautiously from the burette until the last traces of blue colour are removed from the copper solution and the precipitate is of a distinct red colour; the details of the operation are described more fully in § 79.

Suppose that 40 dm. of the diluted urine have been required to reduce the 10 dm. of copper solution, that quantity will have contained 0·5, i.e.,  $\frac{1}{2}$  grn. sugar; but, the urine being diluted 20 times, the 40 dm. represents only 2 dm. of the original urine; therefore 20 grains of it contain  $\frac{1}{2}$  grn. sugar, or 30 grains per 1000.

#### 11. Estimation of Albumen.

a. By Weight. 100 dm. of the clear urine, or less than that quantity if much albumen is present, the 100 dm. being made up with water, are introduced into a good-sized beaker, and heated in the water bath for half an hour. If the urine is sufficiently acid, the albumen will be separated in flocks. Should this not be the case at the end of the half-hour's heating, and the fluid merely appears turbid, one or two drops (not more, unless the urine is alkaline) of acetic acid are added and the heating continued until the albumen separates in flocks; the beaker is then put aside till the precipitate has settled, and the clear liquid passed through a small filter, (previously dried at 212°, then cooled between two watch glasses held together with a spring clip, and weighed;) the precipitate is then washed with a little hot water, and brought upon the filter without loss, the beaker washed out with hot distilled water, and the last traces of precipitate loosened from the sides with a feather. The filter with its contents is then repeatedly washed with hot water, until a drop of the filtrate evaporated on a piece of glass leaves no residue. The funnel containing the filter is then

put into a warm place to dry gradually ; lastly the filter removed into one of the watch glasses and dried thoroughly in the air bath at 220° Fahr. ; another watch glass is then covered over that containing the filter, the spring clip passed over to hold them together, the whole cooled under the exsiccator and weighed ; the weight of the glasses, filter, and clip deducted from the total, gives the weight of albumen in 1000 grains of urine, supposing 100 dm. has been originally taken.

b. By Measure. In order to avoid the tedious process of estimating the albumen as just described, Bödeker has devised a method of titration which gives very fair approximate results. The principle is based on the fact that ferrocyanide of potassium completely precipitates albumen from an acetic acid solution in the proportion of 1 eq. ferrocyanide (=211) to 1 eq. albumen (=1612.)

The standard solution of ferrocyanide is made by dissolving 13.09 grains of the pure salt in 10,000 grains of distilled water. 1 dm. of the solution so prepared precipitates 0.1 grn. albumen.

Process : 50 dm. of the clear filtered urine are mixed with 50 dm. of ordinary commercial acetic acid, and the fluid put into a burette. Five or six small filters are then chosen, of close texture, and put into as many funnels, then moistened with a few drops of acetic acid, and filled up with boiling water ; by this means the subsequent clear filtration of the mixture is considerably facilitated. 10 dm. of the ferrocyanide solution are then measured into a beaker, and 10 dm. of the urinary fluid from the burette added, well shaken and poured upon filter No. 1. If the fluid which passes through is bright and clear with yellowish colour, the ferrocyanide will be in excess, and a drop of the urine added to it will produce a cloudiness. On the other hand, if not enough ferrocyanide has been added, the filtrate will be turbid, and pass through very slowly ; in this case, frequently both the ferrocyanide and the urine will produce a turbidity when added. In testing the filtrate for excess of ferrocyanide, care must be taken not to add too much

of the urine, lest the precipitate of hydroferrocyanide of albumen should dissolve in the excess of albumen.

According to the result obtained from the first filter, a second trial is made, increasing the quantity of urine or ferrocyanide half or as much again, and so on until it is found that the solution first shown to be in excess is reversed; a trial of the mean between this quantity and the previous one will bring the estimation closer, so that a final test may be decisive.

Example: 50 dm. of urine, passed by a patient suffering from Bright's disease, were mixed with the like quantity of acetic acid, and tested as follows:—

Urine.	Ferrocyanide.	In filtrate	
		Urine.	Ferrocyanide.
		gave	
1. 10 dm.	10 dm.	0	prec.
2. 10 "	20 "	prec.	0
3. 10 "	15 "	0	prec.
4. 10 "	17·5 "	0	faint prec.
5. 10 "	18 "	0	0

Therefore, the 10 dm. of diluted urine=5 dm. of the original secretion, contained 1·8 grn. albumen, or 36 grains per 1000.

### 12. Estimation of Soda and Potash.

50 dm. urine are mixed with the same quantity of baryta solution, allowed to stand a short time, and filtered; then 80 dm.=40 dm. urine, measured into a platinum dish and evaporated to dryness in the water-bath; the residue is then ignited to destroy all organic matter, and when cold dissolved in a small quantity of hot water, carbonate of ammonia added so long as a precipitate occurs, filtered through a small filter, the precipitate washed, the filtrate acidified with hydrochloric acid and evaporated to dryness, then cautiously heated to expel all ammoniacal salts. The residue is then treated with a little water and a few drops each of ammonia and carbonate of

ammonia, filtered, the filter thoroughly washed, the filtrate and washings received into a tared platinum dish, then evaporated to dryness, ignited, cooled, and weighed.

By this means the total amount of mixed chlorides of sodium and potassium is obtained; the proportion of each is found by titrating for the chlorine as in § 75, *h*, and calculating as there directed under the head of "mixed alkaline chlorides."

### 13. Estimation of Total Solid Matter.

The correct determination of the total solid matter is a very difficult task, owing to the fact that on the one hand the residue is very hygroscopic, and on the other, that a partial decomposition of the urea takes place by heating it to a sufficient temperature to expel all the water. A tolerably satisfactory plan is to measure 5 dm. into a shallow platinum or porcelain capsule, which is placed beside a vessel of strong sulphuric acid, under the receiver of a powerful air-pump, and kept *in vacuo* until all moisture is removed.

A rough estimation may be made by evaporating 10 or 20 dm. of the urine on the water-bath, then drying in the air-bath at 230° Fahr., until the weight remains tolerably constant.

The only correct method is to introduce a measured portion of the urine, not more than 3 or 4 dm., (contained in a small boat-shaped capsule, filled with fragments of glass,) into a wide glass tube passing through boiling water, to one end of which is attached an aspirator, to the other a chloride of calcium tube; between the aspirator and the tube containing the urine, a small flask is inserted containing a measured quantity of normal sulphuric acid, so that any ammonia, given off in the evaporation, is retained, and its quantity afterward found by titration with normal alkali: it is then calculated into urea, and its weight added to the dry residue actually found. For further details see Neubauer's paper in the "Zeitschrift für An Chemie," part ii, p. 166.



#### 14. Estimation of the Total Saline Matter.

A measured portion of the urine, say 10 dm., is evaporated to dryness in a small porcelain crucible, about 10 drops of nitric acid added, and the crucible gradually heated to dull redness; it is then suffered to cool, and the same quantity of nitric acid again added; then heated up again gradually to a moderately strong heat until all the carbon is destroyed and the residue white; it is then cooled and weighed.

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### ANALYSIS OF SOILS.

§ 81. THE following instructions for the examination of soils are not given so much for the use of practised scientific chemists as for the guidance of those who may not have the advantage of a complete laboratory, or who may only desire to estimate some of the principle constituents of a soil.

The instructions for mechanical analysis, the importance of which cannot be overrated, are taken from Dr. Noad's article on soils in the "Chemist and Druggist," and for whose lucid and most valuable scientific publications of various kinds, more especially on practical analysis, the writer has always had the highest esteem.

#### Mechanical Analysis of a Soil.

a. Selection of the Sample. Too much care cannot be taken to obtain a fair average specimen. For this purpose one or two pounds should be taken from each of four or five different parts of the field where the soil appears to be nearly the same. These should be well mixed together, and a pound

or so selected for analysis; all samples should be kept in well-corked bottles. It is not unfrequent to see in a field otherwise fertile, a few patches almost barren, where plants, especially when the field is in white crop, spring up, and for a time look quite healthy, but soon become diseased, assume a yellow colour, and die. Specimens from such parts should on no account be mixed with the rest; they should be examined by themselves, and the results compared with those given by the fertile parts: by following this course the cause of sterility and the means of curing it are most likely to be discovered.

b. Determination of Water. Spread a weighed quantity (say half a pound) of the soil upon a sheet of white paper, and expose it to the air in a dry room for several hours, weighing it at intervals of two or three hours till the weight remains constant: the loss indicates the amount of water which has evaporated, but by no means the whole of the water which the soil contains. To determine which, heat about 500 grains of the air-dried soil in a small glass beaker plunged into an oil bath, the temperature of which is kept between 300° and 350° Fahr., till it ceases to lose weight, the result gives a close approximation to the amount of water. *Absolute* dissiccation cannot, however, be accomplished except at a heat close upon redness, which is, of course, inadmissible, as the organic matters the soil contains would thereby become altered or destroyed.

c. Absorbing power. Allow the 500 grains of soil dried as above to cool in a covered vessel; then spread it out on a sheet of paper, and expose it to the air for 24 hours; note the increase of weight which is due to absorption of water, and if it amounts to 10 grains, it is so far an indication of great agricultural capability.

d. Power of holding water. Put 1000 grains of air-dried soil into a filter enclosed in another, placed in a funnel; pour cold water, drop by drop, on the soil until it begins to trickle down the neck of the funnel; cover with a piece of glass, and allow it to stand for an hour or two, adding a few

drops of water from time to time until it is certain that the whole soil is perfectly soaked; remove the filters from the funnel, and open them upon a linen cloth to remove the drops of water adhering to the paper. The outside filter is now placed in one pan of the balance, and the inner one containing the soil on the other; and the whole being carefully balanced, the true weight of the wet soil is obtained: suppose this to be 1400, then the soil is capable of holding 40 per cent. of water.

*e.* Rapidity of Drying. Expose the soil with its filter on the plate to the air for 4, 12, or 24 hours, weighing from time to time. The loss of weight, indicating the tendency of the soil to dry, may convey useful information as to the necessity or otherwise of drainage.

*f.* Relative proportions of Gravel, Sand, and Clay. Rub a quantity of air-dried soil between the hands, and remove and weigh any *stones* which may be present. Weigh off 4,000 grains, and pass them through a sieve (No. 1) of copper wire gauze, the meshes of which are about  $\frac{1}{16}$ th of an inch in diameter. Remove the sieve from its bottom, and place it over a deep evaporating basin; throw a gentle stream of water upon the contents, and stir with a spatula or the hand until the water passes through clear. Transfer the residue to another basin, and place it in the water-oven to dry; then weigh, after which ignite in the air, and when cold weigh again. The first weighing gives the amount of *coarse gravel*, and the second indicates the proportion of *organic matter* which this gravel contains. Transfer the soil which has passed through sieve No. 1 to sieve No. 2, the meshes of which are about  $\frac{1}{30}$ th of an inch in diameter, treat the residue on the sieve precisely as before, dry at  $212^{\circ}$ , weigh, ignite, and weigh again; the results give the amount of *gravelly sand*, and of organic matter mixed with it. Dry a portion of the soil which has passed through sieve No. 2 in the water oven, and weigh off 500 grains; transfer to a deep basin or flask, and boil for 20 minutes or so with water. The boiling must be continued until all the par-

ticles are thoroughly separated from each other. The *coarse sand*, *fine sand*, and *finely divided particles* are then separated from each other by the following simple process, recommended by Schultz:—The boiled soil is allowed to cool, and is then washed into an *elutriating glass*, which is merely a tall champagne glass 7 or 8 inches deep and about  $2\frac{3}{4}$  inches wide at the mouth, round which is fastened a brass ring about half-an-inch broad, with a tube slightly inclined downwards proceeding from its side. A gentle stream of water is caused to pass continuously into the elutriating glass in such a manner as to cause a constant agitation of the particles, whereby the finest are washed away through the tube at the top of the glass, and received in a beaker or any other convenient vessel. This stream of water is best kept up and regulated by causing it to flow from a reservoir provided with a stop-cock, to which is attached a tube funnel from 12 to 18 inches long, drawn out to a point, with a fine aperture. The end of this tube is placed nearly at the bottom of the elutriating glass, and the supply of water so adjusted that the funnel tube always remain half full of water. When the water runs off from the discharge tube nearly clear, the stop-cock of the reservoir is closed, and the elutriating glass being removed, the water is decanted from it, and it is washed into a small dish, where it is dried and weighed, after which it is ignited and weighed again; the two weights give the proportion of *coarse sand* and its *organic matter*. The elutriated turbid fluid is allowed to stand for several hours, and the water is then poured off into another beaker. The deposited matter, consisting of *fine sand* and *fine soil*, is then subjected to a second elutriating process, conducted as before, except that the force and volume of the washing water is considerably lessened. The operation is continued until the wash water passes off quite clear; this sometimes takes three or four hours, but it is, with the arrangement described, a self-acting process, requiring no personal superintendence. The residue in the elutriating glass is *fine sand*,

which, with its organic matter, is estimated as before, by drying, weighing, igniting, and re-weighing. We have only now to deduct from the original 500 grains the quantities of *coarse* and *fine sand*, to obtain the proportion of finely-divided matter. The results of this mechanical analysis may be tabulated thus, (Schultz):—

100 parts of the soil, dried at 212° Fahr., contain (for example)—

		Fixed Substances.	Combustible or Volatile Substances.
6.90	{ Gravel (coarse).....	6.90	0.00
	{ Organic matter.....	...	...
7.10	{ Gravel (fine).....	6.43	...
	{ Organic matter.....	...	0.67
35.50	{ Sand (coarse) .....	34.37	...
	{ Organic matter.....	...	1.13
40.00	{ Sand (fine) .....	38.50	...
	{ Organic matter.....	...	1.50
10.50	{ Fine soil .....	9.50	...
	{ Organic matter, ammonia and combined water .....	...	1.00
100.00		95.70	4.3

Stones, 2.10 per cent.

This mechanical treatment of soils is of high importance, and it is to be regretted that so few of our English soils have hitherto been so examined. The same remark applies to the analysis of *clays*. The operations above described apply equally to *clays* and to *soils*, except that in the case of *clays* we have not to look for *gravel*.

To render the matter complete, however, the gravel and sand should be moistened and examined under the microscope, with the view of ascertaining if they are wholly siliceous, or if they contain also fragments of different kinds of rock—sandstones,

slates, granites, traps, limestones, or ironstones. A few drops of strong hydrochloric acid should also be added, when the presence of limestone is shewn distinctly by an effervescence of peroxide of iron by the brown colour which the acid speedily assumes; and of black oxide of manganese by the smell of chlorine, which is easily recognized.

*g.* Determination of the Density of a Soil. Dry a sample of the soil (from which the large stones have been picked out) at  $212^{\circ}$  in the water oven till it ceases to lose weight. Fill a perfectly clean and dry common phial with distilled water up to a mark made with a file on the neck, and weigh it carefully. Pour out part of the water, and introduce into the bottle in its stead 1,000 grains of the dried soil; shake the bottle well, to allow the air to escape from the pores of the soil; fill up again with water to the mark on the neck, and again weigh. The weight of the soil divided by the difference between the weight of the bottle with soil and water, and the sum of the weights of soil and the bottle of water together, gives the density or specific gravity. Example—

	Grains.
The bottle with water alone weighs .....	2,000
The dry soil .....	1,000
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Sum (being the weight which the bottle with the soil and water <i>would have had</i> , could the soil have been introduced without dis- placing any of the water) .....	3,000
Actual weight of soil and water .....	2,600
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Difference (being the weight of water taken out to admit 1,000 grains of soil) .....	400

Therefore, 1,000 grains of soil have the same *bulk* as 400 grains of water: i.e., the soil is  $2\frac{1}{2}$  times heavier than the water, since  $\frac{1000}{400} = 2.5$ , its specific gravity.

*h.* Determination of the Absolute Weight. Weigh an exact imperial half-pint of the soil in any state of dryness. When this weight is multiplied by 150 it will give very nearly the weight of a cubic foot of the soil in that state.

#### Chemical Analysis.

The accurate and complete quantitative analysis of soils is a work of some difficulty, and cannot be entirely accomplished by volumetric means. Many of the principal substances, however, may be estimated in this manner, and the following method of procedure is given as the most convenient :—

1. Water. 250 grains of the air-dried sifted soil are weighed in a porcelain, platinum, or iron crucible, and heated for a considerable time in the water bath till the weight is constant. The loss represents the amount of water.

2. Organic matter. 50 grains of the residue from 1 are ignited in a platinum or porcelain crucible until all the organic matter is destroyed; the residue is then suffered to cool, moistened with solution of carbonate of ammonia, (to re-carbonate any lime,) then dried in the air bath at about 300° Fahr.; the loss indicates the amount of organic matter in the perfectly dry soil, which is then calculated for 100 parts of air-dried soil.

3. Carbonic Acid. 50 grs. of the air-dried soil are introduced into the apparatus, Fig. 12, and the carbonic acid estimated as in § 22.

4. Chlorine. 250 grs. of the air-dried soil are burnt in a platinum crucible, then cooled and moistened with a solution of nitrate of potash, again heated gently to dryness, then ignited again. The cold residue is then lixiviated with boiling water, filtered, the filtrate neutralized with acetic acid, and a measured portion of it titrated with  $\frac{N}{10}$  silver and chromate of potash, as in § 74.

5. Oxide of Iron. The insoluble residue of 4=250 grs. soil, is heated in the water bath with pure hydrochloric acid to

extract all soluble matter, the solution filtered off, the residue washed with boiling water on a filter, (residue preserved for future examination,) and the filtrate and washings collected and diluted to 500 dm. 200 dm.=100 grs. soil, are then taken, heated with a little nitric acid to peroxidise all the iron, and ammonia added in excess, so as to precipitate all oxide of iron and alumina; if the latter be required to be estimated, the precipitate must be collected on a filter, well washed, putting the filtrate and washings aside, then dried, ignited, and weighed; the residue, consisting of oxide of iron and alumina, with whatever traces of phosphoric acid there may be, is redissolved in a little hydrochloric acid, the solution treated with zinc, diluted considerably, and titrated with  $\frac{N}{10}$  bichromate, § 44, for oxide of iron, the quantity so found deducted from the total weight of the precipitate gives the alumina and phosphoric acid. Should the estimation of alumina not be required, the precipitate need not be ignited, but simply redissolved with hydrochloric acid on the filter and titrated at once for iron. Should any portion of the iron in the original soil exist as protoxide, a weighed quantity, say 100 grains, of the fresh, sifted, and non-ignited soil is exhausted with pure hydrochloric acid, the solution filtered and titrated direct with bichromate, as in § 48.

6. Lime. The filtrate and washings from 5=100 grs. soil, are mixed with oxalate of ammonia in excess, the solution set aside in a warm place for an hour or so, the precipitate then collected on a filter, well washed, dried, and together with the filter ignited. The mixture of carbonate and caustic lime thus obtained is dissolved in an excess of normal nitric acid, and titrated as in § 18; calculation for lime to be made as there directed.

7. Magnesia. The filtrate and washings from 6=100 grs. soil, which if bulky must be evaporated somewhat in the water bath, is to be made freely alkaline with ammonia, arseniate of ammonia added in slight excess, and the solution set aside for twelve hours in the cold, that the magnesia may be precipi-



tated as double arseniate of ammonia and magnesia. The precipitate collected on a filter well washed with ammoniacal water, (filtrate and washings set aside,) redissolved on the filter with acetic acid, and the solution titrated with uranium as in § 64, 3; see also §§ 78, 1 and 38. 1 dm. of standard uranium solution represents 0.0563 grn. Mg O.

8. Alkalies. The filtrate and washings from 7=100 grs. soil, containing the alkalies as chlorides, together with chloride of ammonium and a small quantity of arseniate of ammonia, is evaporated to dryness on the water bath, then ignited gently and carefully under a chimney to volatilize all the arseniate and other salts of ammonia. The alkalies are then left nearly pure as chlorides; the residue is dissolved in a very little water, filtered through a small filter into a small crucible, evaporated to dryness, and weighed direct. If it be desirable to ascertain the amount of potash, it may be separated by weight as double chloride of platinum and potassium, or the indirect method of calculation, as in § 75, *h*, may be adopted.

9. Phosphoric Acid. The remainder of the acid solution, viz., 300 dm.=150 grs. soil, is mixed with a little nitric acid, heated and precipitated with ammonia, as in 5, the precipitate collected on a filter and washed with boiling water, (filtrate and washings set aside,) the precipitate is then dissolved on the filter with dilute nitric acid, the filter slightly washed, and the solution so obtained digested in the water bath for twenty-four hours with about two ounces of the fluid prepared as follows:

Molybdic acid .....	100 grains
Solution of Ammonia, .900 .....	100 dm.
Pure nitric acid, about 1.30 .....	150 dm.

If any precipitate occurs it will contain all the phosphoric acid (unless it should exist in large quantity, which is not probable) as phospho-molybdate of ammonia, which is to be collected on a small filter, well washed with the same fluid, then redissolved in ammonia, and a portion of the magnesia mixture added,

§ 78, 1, to precipitate the phosphoric acid as double phosphate of magnesia and ammonia; the precipitate so produced is dissolved in acetic acid, and titrated with uranium as in § 78, 1.

10. Sulphuric Acid. The filtrate and washings from 9 = 150 grs. soil, are diluted up to a definite measure, and a convenient portion titrated for sulphuric acid by any of the methods given in § 28.

11. Ammonia. From 200 to 500 grains of the fresh air-dried soil are introduced into the distilling flask, Fig. 11, together with a little water and a small piece of bees' wax, (to prevent frothing,) the tube *d* is filled with strong caustic potash or soda, the whole of which is allowed to run into the flask as soon as the heating commences. In all other respects the operation is conducted as described in § 16.

12. Nitrogen. 100 grains of the soil are dried at 300° Fahr., and when cold mixed with soda lime in a combustion tube, and ignited as usual, § 17. The ammonia evolved may be received into normal sulphuric acid, and the mixture afterwards titrated with normal alkali in the usual manner; or dilute hydrochloric acid may be used in the bulb apparatus, the fluid evaporated to dryness on the water bath, then heated in the air bath to 240° Fahr., and the residual chloride of ammonium titrated as in §§ 40, 75.

13. Residue insoluble in Hydrochloric Acid. The insoluble matter which has already been collected, as in 5 = 250 grs. soil, and consisting mainly of insoluble silicate of alumina and sand, is transferred to a platinum or porcelain dish or large crucible, dried and mixed with sulphuric acid of about 1.6 spec. grav. in excess; the mixture is left to digest somewhat, then heated slowly under a hood, to drive off all the free acid; the residue is then cooled, lixiviated with water, filtered, and the filtrate precipitated with ammonia; the precipitate may be washed, dried, ignited, and weighed as "Alumina insoluble in Hydrochloric Acid." The insoluble residue will consist of pure quartz sand.

## ANALYSIS OF MANURES.

## GUANO.

§ 82. 1. Moisture. 100 grains, weighed in a platinum or porcelain crucible, are dried in the water bath till the weight is constant, the loss gives the percentage of moisture.

2. Total Fixed Constituents. Residue of 1=100 grains guano are ignited at a low red heat till all organic matter is destroyed, and the residue of a white or greyish colour; the loss of weight gives the percentage of fixed constituents, which will act as a control over the subsequent analysis.

3. Sand, Clay, or other Insoluble Matter. Residue of 2 is boiled with dilute hydrochloric acid (which should not cause any amount of effervescence) till all soluble matter is extracted, the solution filtered, residue brought on the filter, washed, dried, ignited, and weighed, gives the percentage of insoluble matter. The filtrate and washings containing all the soluble matters are diluted up to a definite measure, say 500 dm.

4. Phosphoric Acid. 200 dm. of the solution prepared as in 3=40 grains guano are precipitated with ammonia in excess, the precipitate of phosphate of lime and magnesia redissolved in acetic acid, and the solution divided in half, one portion titrated with uranium for phosphoric acid, as in § 78, 1, the remainder set aside for

5. Lime. To half of the acetic acid solution prepared as in 4, sufficient oxalate of ammonia is added to precipitate all the lime; after standing an hour or so, the supernatant liquid is filtered off and the precipitate washed, (reserving the filtrate and washings,) then dissolved and titrated as in § 60, 1.

6. Magnesia. The filtrate and washings from 5 are rendered alkaline with ammonia, set aside for 12 hours, the precipitate of double phosphate of magnesia and ammonia collected, dissolved, and titrated as in § 38.

7. Alkalies. The filtrate and washings from 6 are mixed with sufficient baryta water to remove all the phosphoric and sulphuric acids; the precipitate removed by filtration; the filtrate evaporated to a small bulk, and treated with carbonate and caustic ammonia, to remove excess of baryta, and the filtrate and washings from this precipitate acidified with hydrochloric acid, evaporated to dryness, ignited, then redissolved in a small quantity of water, a few drops each of ammonia and carbonate of ammonia added, filtered into a weighed platinum or porcelain crucible, the small filter thoroughly washed, and the filtrate and washings evaporated to dryness, ignited, and weighed as chlorides.

For the estimation of potash and soda contained in the mixture see § 80, 12, which also contains rather more minute directions for the careful separation of the alkaline salts by the above method.

8. Ammonia. 10 grains of the guano, or more, if poor in ammonia, are boiled with caustic potash in the distilling apparatus, Fig. 11, and the estimation of ammonia conducted as described in § 16.

9. Nitrogen and Ammonia. From 5 to 10 grains of the guano, according to its quality, are dried in the water bath and carefully mixed with soda lime, (previously coarsely powdered, heated, and cooled,) and the mixture introduced into a hard glass tube, closed at one end, about fourteen inches long and half-an-inch diameter, the closed end is previously filled to about three quarters of an inch with a dried mixture of equal parts oxalic acid and soda lime; on the top of this the mixture of guano and soda lime is filled in to within one and a half inches of the open end; a loose plug of dry asbestos is then introduced, and a good fitting cork, carrying the Varrentrapp and Will's bulb apparatus, (filled to the proper extent with normal sulphuric acid,) inserted. The tube is then placed in the gas or charcoal combustion furnace, and gradually heated from its open end downwards until the

ammonia is nearly all evolved; the whole tube is then strongly heated, and the heat brought especially to bear on the lower end containing the mixture of oxalic acid and soda lime; by this means a strong current of carbonic acid is produced, which drives out all the ammonia into the acid; when this strong current ceases somewhat, and before the acid has opportunity to regurgitate into the hot exhausted tube, the cork is removed, the acid solution emptied into a beaker, the bulbs washed out into the same vessel, the mixture filtered, if necessary, and the excess of acid ascertained by titration with normal alkali, as in § 12, p. 29. Each dm. of acid found to be combined with ammonia represents 0.17 gra. of that substance, or 0.14 gra. nitrogen.

#### Phosphatic Manures.

Moisture and fixed constituents are determined as in the case of guano.

100 grains of the manure are lixiviated with warm water, allowed to settle, the clear liquid passed through a filter; the operation repeated, the residue boiled once or twice with water, the fluid being decanted through the same filter, the residue is then mainly brought upon it and well washed with boiling water; the filtrate and washings so obtained are diluted to 500 dm., set aside and marked "Aqueous solution," 100 gra. manure.

The insoluble residue on the filter is pushed through the funnel into the beaker in which it was originally digested, the filter treated with warm dilute hydrochloric acid, washed with boiling water into the beaker, a good quantity of hydrochloric acid added, and the whole digested for some time at near boiling heat. The clear acid fluid is then passed through a filter, the insoluble residue brought upon it and washed till all soluble matter is removed, filtrate and washings then diluted to 500 dm., set aside and marked "Acid solution," 100 gra. manure.

The insoluble residue on the filter is dried, ignited, and weighed, as sand, clay, &c.

In the aqueous solution, phosphoric acid, lime, and alkalies are determined as in the case of guano; sulphuric acid as in § 28, 3.

In the acid solution, which contains traces of iron, and probably alumina, the phosphoric acid is separated and estimated as recommended in § 78, 1. Lime and sulphuric acid as in the aqueous acid solution; oxide of iron, if necessary, by bichromate as in § 81, 5.

Ammonia and nitrogen as in guano.

In subsequently calculating the results, the phosphoric acid found in the aqueous solution is added to the lime in the proportion of 71 to 28, the remainder of the lime to the sulphuric acid in the proportion of 28 to 40; remainder of the sulphuric acid to the alkalies, unless existing in the manure as chlorides; any sulphuric acid over and above this is entered as existing in a free state.

In the acid solution, the phosphoric acid is added to the lime in the proportion of 71 to 84, ( $3 \text{ Ca O}, \text{PO}_5$ ) remainder of lime to the sulphuric acid in the proportion of 28 to 40, both of which should pretty nearly agree.

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#### ANALYSIS OF WATER.

§ 83. Most of the ordinary constituents of spring or river waters may readily be estimated by volumetric methods, and owing to the comparatively pure state in which they occur, can, in the hands of good manipulators, be very accurately determined. Three systems of measurement are open to the operator, viz., the litre, the imperial pint, or the 1000 dm. measure, the

two latter being respectively one-eighth and one-seventh of the imperial gallon.

1. Total Solid Matter. 1000 dm. of the water, (= one-seventh of a gallon,) or if the operator prefers it, one imperial pint, (to either of which from 10 to 20 dm. of normal carbonate of soda, § 11, otherwise 5 or 10 grains of pure and dry carbonate of soda in powder is added,) is slowly evaporated, preferably in a weighed platinum dish, at first over a gas lamp, then on the water bath to complete dryness; taking care during the operation that no loss occurs by bubbling or spirting. The dish is then placed in an air bath and heated to 300° Fahr. till the weight is constant. The weight so obtained, minus the carbonate of soda added, represents the total amount of solid matter, which can be calculated for the imperial gallon = 70,000 grains, and serves as a control over the subsequent analysis.

2. Organic Matter. The platinum dish containing the residue of 1 is placed over a spirit or gas lamp, and slowly heated to dull redness, until the blackening of the residue which first appears, is totally removed, (should this take place rapidly, and with faint scintillation, the presence of alkaline nitrates may be inferred;) the dish is then cooled, strong carbonic acid water or a little solution of carbonate of ammonia added, evaporated, gently ignited, then cooled under the exsiccator, and quickly weighed; the loss between this second weighing and that of No. 1 is generally considered to represent the amount of organic matter of vegetable or animal origin, or mixtures of both, which was originally present in the water, and which has been dissipated by the ignition.

3. Total Amount of Carbonic Acid. This can only be done accurately by quietly collecting the water at its source, in bottles containing a measured excess of pure chloride of calcium and ammonia, (free from carbonic acid,) collecting the precipitate, and titrating with nitric acid as in § 22, *a*. In most cases the method of procedure given in § 22, *b*, is sufficient.

The total amount of *combined* carbonic acid may also be found in the residue of 2 as follows :—

20 dm., or more if necessary, of normal nitric acid are added to the residue in the platinum dish, which should be covered, to prevent loss by effervescence; the mixture digested warm till dissolved, then a few drops of litmus added, and titrated with normal alkali for the excess of nitric acid; the quantity so found is deducted from the total used, then as much deducted from that as would be required to neutralize the weight of carbonate of soda added in 1; the remainder multiplied by 0.22 will give the weight of carbonic acid combined with the lime, magnesia, and alkalies, (if any,) as monocarbonates.

4. Carbonic Acid combined with Alkalies. 1000 dm. of the water are boiled in a flask for an hour, to precipitate the earthy carbonates, which are filtered off, and slightly washed with boiling water; the filtrate is divided into two equal parts, *a* and *b*; *a* is titrated with  $\frac{N}{10}$  silver and chromate of potash, as in § 74, for the amount of chlorine; *b* is slightly acidified with hydrochloric acid, evaporated to perfect dryness, gently ignited, redissolved in a little hot water, diluted to the same bulk as *a*, and titrated for chlorine as before; the increase of chlorine found in this case represents the amount of alkali existing as carbonate. If therefore the number of dm. of  $\frac{N}{10}$  silver, used in excess of *a*, be multiplied by 0.022, the weight of carbonic acid in combination with alkali will be obtained.

**Estimation of the Lime, Magnesia, Silica, Alumina, and Oxide of Iron.**

5. Silica. Four imperial pints, or 4000 dm. (less, if the water is fully impregnated with mineral matter,) are slightly acidified with hydrochloric acid, and evaporated in a place free from dust, first in a large porcelain dish, and lastly in a platinum vessel, to dryness, the residue is well dried, and dissolved in a small quantity of dilute hydrochloric acid, the solution filtered,



to collect the flocculent silica, which is washed with the rinsings of the dish, lastly with pure water, dried, ignited, and weighed in a covered crucible.

6. Oxide of Iron and Alumina. The filtrate from 5 is heated, and rendered alkaline by ammonia, by which means the oxide of iron and alumina are precipitated. If the iron alone is to be determined, the precipitate after washing may be redissolved and titrated with permanganate. If the alumina is also to be determined, the washed precipitate must be dried, ignited, and weighed, before estimating the iron, just as in § 81, 5.

7. Lime. The filtrate from 6 is mixed with oxalate of ammonia in slight excess, and set aside in a warm place to settle thoroughly. The precipitate of oxalate of lime is then collected, well washed, (reserving the filtrate and washings,) then titrated with permanganate, as in § 60, 1, or dried and ignited, to convert it into a mixture of carbonate and caustic lime, which may be titrated residually with normal nitric acid and alkali, as in § 18.

8. Magnesia. The filtrate and washings from 7, concentrated somewhat by evaporation, are rendered alkaline with ammonia, some phosphate of soda added, and the precipitated double phosphate of magnesia and ammonia titrated as in §§ 38, 78, 1; each decem of uranium solution representing 0.0563 grn. magnesia.

9. Chlorine. From 100 to 500 dm. of the original water are evaporated somewhat, and titrated with  $\frac{N}{10}$  silver and chromate of potash, as in § 74.

10. Sulphuric Acid. 500 or 1000 dm. are evaporated to one-fourth the bulk, and the amount of sulphuric acid found by any of the methods in § 28.

11. Alkaline Salts. 2000 dm. or two imperial pints of the water are evaporated to one-fourth their bulk in a porcelain dish, a little chloride of barium is then added, together with baryta water in sufficient quantity to render the mixture dis-

tinctly alkaline, the fluid is then filtered off through a somewhat porous filter, and the precipitate slightly washed. The clear filtrate and washings are then treated with carbonate and caustic ammonia to remove excess of baryta, again filtered, washed, evaporated to perfect dryness, and gently ignited to expel all ammoniacal salts; the residue is then dissolved in a little hot water, a few drops each of oxalate, carbonate and caustic ammonia added, filtered through a small filter into a weighed platinum crucible or dish, the filter well washed with boiling water, again evaporated, ignited, cooled, and weighed as alkaline chlorides. The indirect separation of the soda and potash can be accomplished as in § 75, *h*.

12. Nitric Acid. This constituent is only found, as a rule, in waters contaminated with sewage matter, its amount may be determined by evaporating a good quantity of the water to a small bulk, and estimating the nitric acid as in § 26, 4, 5, or 7.

Special classes of water containing metals, (such as mine waters,) sulphur, sulphuretted hydrogen, and other unusual constituents require, as a rule, much more complicated methods of treatment than are here given, for which the operator cannot do better than consult the new edition of Fresenius' "Quantitative Analysis."

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#### ESTIMATION OF THE HARDNESS OF WATER.

##### Clark's Method.

§ 84. THE ordinary fresh waters used for drinking, washing, and manufacturing purposes, all contain salts of lime, and some of them salts of magnesia, free carbonic acid, alumina, and oxide of iron, all of which have the property of rendering the water *hard*, that is to say, instead of giving a free lather with

soap like rain or soft water, it decomposes the soap into a greasy, dirty scum, consisting of stearate of lime or magnesia, &c., and until an amount of soap has been added, sufficient to combine with all these salts, no soft lather will be produced, nor will any detergent power be exerted by the liquid. The late Prof. Clark, of Aberdeen, devised a method of examination, based upon the soap reaction above mentioned, which has come into very general use, and is extremely serviceable as a ready means of ascertaining the amount of earthy salts contained in water used for generating steam, or for general domestic, and manufacturing purposes.

a. Preparation of Standard Water. In order to conduct the examination of any given water in a proper manner, it is first necessary to prepare a standard water containing a known quantity of lime in solution. This is best done by dissolving 27.5 grains of crystallized gypsum, (Selenite,) previously reduced to fine powder, in one imperial gallon (70,000 grains) of distilled water. This weight of sulphate of lime is equal to 16 grs. of carbonate of lime, and the water so prepared is called by Clark—"standard water of 16° hardness," each grain of carbonate of lime, or a proportionate weight of any other lime salt in the gallon, being considered as one degree of hardness. Clark directs his standard solution to be made by dissolving 16 grains of Iceland spar ( $\text{CaO}, \text{CO}_2$ ) in hydrochloric acid, evaporating to dryness, then diluting to one gallon; but as this is somewhat troublesome and liable to loss from effervescence, the crystallized sulphate is preferable.

b. Preparation of the Standard Soap Solution. This solution is directed by Clark to be prepared by dissolving hard curd soap in proof spirit by the aid of heat; but as a very unsatisfactory liquid is produced by this means, owing to the constant precipitation of flocky matter and carbonate of soda at ordinary temperatures, I have for some time used a solution of the pure potash soft soap in proof spirit, with advantage.

This soap, which is known as the pure soft soap of the London Pharmacopæia, can readily be obtained, and the solution made with it may be kept any length of time without undergoing change. It is prepared by simply digesting a convenient quantity of the soap with a mixture of equal volumes of alcohol (pure or methylated) and distilled water at ordinary temperature until dissolved. If not completely clear it may be passed through a filter.

The solution so prepared must now be titrated by the help of the standard water, and here I prefer to use the modification suggested by Pierce Wilson, ("Ann. Chem. u. Pharm.," 119, 318,) which enables the operator to dispense with the table constructed by Clark, and which was rendered necessary by the fact that in order to produce a persistent lather an excess of soap to the extent of 1.5 dm. was required. This difficulty appears to be entirely overcome by adding a certain quantity of carbonate of soda so as to soften the water to the extent necessary for the prevention of an excess of soap.

c. Titration of the Soap Solution. 100 dm. of the standard water are measured into a stoppered bottle holding about 6 oz.; 4 dm. of cold saturated solution of carbonate of soda added, and the soap solution immediately delivered in from a Mohr's burette, until a point occurs when by a few vigorous shakes a soft and copious lather is produced, which will remain for at least five minutes. The quantity of soap solution required to produce this should be exactly 32 dm.; therefore, if on trying the solution *b*, 30 or 31 dm. have been necessary, it must be diluted with proof spirit so that exactly 32 dm. are required to produce the lather; if more than 32 dm. have been required, more of the concentrated soap solution must be added until the same strength is gained.

d. Examination of a Sample of Water. 100 dm. of the water are measured into the bottle and well shaken to liberate any free carbonic acid which may be present. The

air in the bottle is then blown out by an india rubber syringe, or sucked out by a bent glass tube; if this precaution were not taken, the gas would decompose a slight portion of the soap solution. 4 dm. of carbonate of soda are added, as in c, and sufficient soap solution cautiously delivered from the burette to produce the permanent lather. Supposing that 20 dm. have been required, the hardness is  $10^{\circ}$ , so that up to 32 dm. half the number of decems of soap required for 100 dm. of water will be the degree of hardness. When the water is more than  $16^{\circ}$ , the carbonate of soda precipitates a portion of the lime out very rapidly, so that the quantity of soap solution is not a correct measure of the amount of earthy matters; consequently in such a case the sample of water must be previously diluted with one or two volumes of distilled water, according to circumstances, then 100 dm. taken for titration, and the quantity of soap solution required doubled or trebled, as the case may be, before taking the half as the amount of hardness.

Example: 100 dm. of water derived from the chalk formation, and containing a very large proportion of lime, was diluted with 200 dm. of distilled water; then 100 dm. of the mixture titrated as above, the quantity of soap solution required was 15.5 dm., which multiplied by 3 gave 46.5 dm.; the degree of hardness was therefore half this = 23.25.

The degree of hardness obtained in this manner represents the total amounts of the hardening constituents of water, but as a portion of these constituents, viz., carbonate of lime and magnesia with free carbonic acid, are removed to a certain extent by boiling, it is sometimes desirable to know the degree of permanent hardness, that is to say, after the water has been boiled. To this end about half a pint of the water is measured into a flask, a small glass funnel inserted into the neck, and the water boiled for an hour, adding fresh distilled water to repair the waste; when cold, the exact measure is made up with distilled water, and 100 dm. titrated as above; the

quantity of soap solution required represents the degree of permanent hardness.

If it be desired to use the cubic centimeter instead of the decem measure, it is only necessary to take 100 CC of the water with 4 CC of soda solution for titration, using a CC burette for the soap solution.

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COMPLETE AND RAPID ESTIMATION OF THE ORDINARY CON-  
STITUENTS OF SPRING OR RIVER WATERS.

§ 85. In the "Quarterly Journal of the Chemical Society" for December, 1862, is published a paper by E. Nicholson, of the Army Medical School Laboratory, Fort Pitt, on a new volumetric method of estimating some of the constituents of fresh waters, which seems to be very serviceable for the purpose intended, namely, the rapid approximate estimation of the usual substance found in drinking waters, for the use of medical men, sanatory inspectors, &c.

I regret exceedingly that owing to its late date I have not had sufficient time to test the process in the most satisfactory manner; it happened, however, that a complete analysis was in hand at the time, of some water taken from a new Artesian well in the neighbourhood of Norwich, 1200 feet in depth, and therefore the opportunity occurred of comparing the results obtained by the best known methods in laboratory use, with those of the new method.

It is to be regretted that the writer of the paper did not give the analysis of the two samples of water examined by him at Fort Pitt, by the ordinary method, side by side with his own.

The whole process is a combination of the methods devised by Prof. Clark for ascertaining the hardness of water, those of Boutron Chalard, and Boudet, adopted in their "Hydro-timétrie," for the estimation of lime, magnesia, and sulphuric

acid, and an ingenious method for estimating the alkaline salts, devised by the author.

The instruments required, are one each of Mohr's and Gay Lussac's burettes, graduated into  $\frac{1}{10}$  CC, each division of which is considered as one degree. Two or three whole pipettes, say one each of 10, 50, and 100 CC, a few basins and beakers, half-a-dozen three-ounce stoppered bottles, and a litre flask.

If the grain system of measurement be preferred, it is only necessary to substitute the decem for the cubic centimeter as the standard.

#### Preparation of the Standard Solutions.

1. Standard Solution of Lime. 0.1 Gm. of the purest Iceland spar is dissolved in a little pure hydrochloric acid, evaporated cautiously to dryness in the water bath, again dissolved in water and evaporated to dryness, then heated to about 230° Fahr., dissolved in distilled water, and diluted to exactly 1 litre. 1 grain of Iceland spar treated in the same way, and dissolved in 1000 dm. of water, will give a solution of the same strength, namely, 7 grains of carbonate of lime in one imperial gallon of water. I prefer to use the crystallized sulphate of lime, (selenite,) as requiring less trouble, the weight in that case being 0.122 Gm. per litre, or 1.22 grn. per 1000 dm.

2. Standard Solution of Soap. Pure potash soft soap of the London Pharmacopœia is dissolved in equal measures of alcohol and distilled water, of such strength that 22 degrees = 2.2 CC will exactly give a permanent lather with 50 CC of the standard carbonate of lime solution. The actual quantity of soap solution required to equal the hardness is 20 degrees, the 2° in excess being necessary to produce the permanent lather. This requisite excess of 2 degrees per 50 CC is to be deducted from all determinations of hardness.

3. Standard Baryta Solutions. *a.* 0.26 Gm. ( $=\frac{1}{30}$  at.) of pure and dry nitrate of baryta is dissolved in 1 litre of water, or 2.6 grn. in 1000 dm. This solution is equivalent in

point of hardness to the standard water No. 1, 50 CC of it, therefore, mark 20 degrees; it is generally advisable, however, to use a stronger solution as follows:—

b. 1.30 Gm. ( $=\frac{1}{100}$  at.) nitrate of baryta is dissolved in 1 litre or 13 grains per 1000 dm., each CC or dm. marking 2 degrees.

4. Standard Nitrate of Silver. 8.5 Gm. ( $=\frac{1}{20}$  at.) of the pure salt is dissolved in 1 litre or 85 grn. per 1000 dm.; each 0.1 CC or dm. representing 1 degree of chlorine. This solution may also be made by diluting  $\frac{N}{10}$  silver, § 74, with an equal bulk of water.

5. Standard Oxalate of Ammonia. 0.355 Gm. ( $=\frac{1}{1000}$  at.) of the pure salt is dissolved in 1 litre or 3.55 grn. per 1000 dm.; each CC or dm. precipitates 1 degree of lime.

6. Standard Permanganate of Potash. This solution is made by dissolving the pure crystals of permanganate in distilled water, of such strength that 1 CC or dm. is exactly required to oxidise the same volume of oxalate of ammonia solution. If the operator possesses the  $\frac{N}{10}$  solution, § 43; 50 CC or dm. of it, diluted to 1 litre or 1000 dm. with distilled water, will give a solution of the proper strength, viz., 0.159 Gm., ( $=\frac{1}{10000}$  at.) pure permanganate per litre.

The above method of graduating the solutions has been adopted by Nicholson, as the important advantage is thereby gained of being able to calculate the quantity of any substance per litre of water, by multiplying the number of degrees obtained in the analysis by the atomic weights of the substance. Thus:—

20 degrees	×	50 (eq. of $\text{CaO}, \text{CO}_2$ )	=	1000 Gm. per litre,
				of Carbonate of lime.
20	„	×	28 (eq. of $\text{CaO}$ )	= 0.560 Gm. per litre,
				of Lime.
20	„	×	35.5 (eq. of $\text{Cl}$ )	= 0.710 Gm. per litre,
				of Chlorine.

And so on.



The quantities thus obtained, when multiplied by 70, show the number of grains per gallon of water. If however the decem and grain system, described in the former part of this book, is used, the 20 degrees  $\times$  50 for carbonate of lime as above, would yield 1 grain of the substance to each 1000 dm. of water, (as in the standard lime solution, for instance,) instead of 1000 Gm. per litre; therefore to preserve the correct absolute weight, the decimal point must be moved one place to the right, and the number multiplied by 7, to give the weight in grains per gallon, since 1000 dm. is the one-seventh part of a gallon. The absolute weight may however be left quite out of the question, if the operator chooses; in which case the same numbers may be used empirically for the grain system, as given above for the gramme.

The following description of the analytical process is taken, with very slight modifications, from Nicholson's paper in the Chemical Society's Journal, p. 472.

#### The Analytical Process.

1. 50 CC of the water to be analysed are measured by the pipette into a stoppered bottle of about three-ounce capacity. The soap solution is gradually dropped in from the burette, the bottle being strongly shaken at intervals, until a lather begins to form on the surface. The soap solution is then added more cautiously, until the water, on agitation, presents an iridescent, large-bubbled lather, breaking down very slowly, and, after a few minutes, leaving the surface perfectly covered with a beady film, reconvertible into a lather on again agitating. After a little practice, the exact point where the lather becomes permanent is attained by the addition of one small drop, about one-sixth of a degree, of soap solution. The process thus indicates the presence of .0005 Gm. per litre of lime.

Two degrees are deducted for the excess necessary to produce a lather. The number of degrees found represents the hardness due to lime, magnesia, iron, and carbonic acid gas. The alkaline salts usually found in water, have no effect on the soap solution.\*

2. The amount of Lime and Magnesia, and, by difference, of free Carbonic Acid Gas, is found by taking the hardness of the water after expulsion of the carbonic acid gas. To this end 50 CC of the water are evaporated to dryness with one or two drops of sulphuric acid, and the residue is ignited to expel excess of acid; if the vapours be offensive, the residue may be neutralized by a few drops of ammonia, before ignition. The residue is dissolved in 50 CC of distilled water, and the hardness is ascertained. Oxide of iron will remain insoluble; its amount is to be deducted from the carbonic acid.

3. The Lime is determined by the well-known application of permanganate of potash to the oxidation of oxalic acid, § 60.

To 50 CC of the water, add 50 CC (or, if the hardness exceeds 50 degrees, 100 CC) of the standard solution of oxalate of ammonia, let the mixture stand in a warm place for an hour, and filter. The filtrate and washings are heated in a basin or flask to about 70° C., (150° Fahr.) with a few drops of sulphuric acid, and the standard solution of permanganate of potash is added from a burette. Subtract the number of CC of permanganate required for oxidation of the excess of oxalic acid, from the number of CC of oxalate of ammonia added to the water: the difference gives the number of degrees of lime.

50 CC of the permanganate solution ought exactly to oxidise 50 CC of the oxalate of ammonia solution.

To 50 CC of the water, ignited with sulphuric acid, as before

\* If the hardness exceed 80 degrees, or if much magnesia be present, the earthy soap often assumes a curdy form, deranging the production of a lather; in this case only 25 CC should be taken for experiment, the 50 CC being made up with distilled water.

described, (2,)\* add 20 CC, or more, of the stronger solution of nitrate of baryta, taking care that the hardness of the quantity added (2 degrees per 1 CC) be much greater than that of the water, as previously ascertained. If no alkaline sulphates are present, the amount of sulphate of baryta precipitated will be exactly equivalent in hardness to the amount of earthy sulphates; and the hardness, when ascertained by the soap solution, will be exactly that of the baryta solution added. If, for example, 20 CC=40 degrees of baryta solution have been added to 50 CC of water containing 35 degrees of sulphate of lime and of magnesia, (total 40+35,) 35 degrees of sulphate of baryta will be precipitated and the hardness will be reduced to 40 degrees, exactly the hardness of the baryta added. But, on the other hand, if sulphate of soda be present in the water, in addition to the earthy sulphates, a greater quantity of sulphate of baryta will be precipitated, and the hardness will be reduced to less than 40 degrees. Should it be reduced to 36 degrees, that will show that 4 degrees of alkaline sulphate were present.†

5. Chlorine is determined in 50 CC of the water by the solution of nitrate of silver, as in § 74. If the quantity be very small, it is best to evaporate 500 CC of the water to a small bulk, and count cubic centimeters as degrees.

6. Sulphuric Acid is determined by adding to 50 CC of the water, 10 CC, or more if necessary, of the stronger baryta solution, and ascertaining by the soap solution the hardness of the mixture. The loss of hardness from the precipitation of

\* It may be as well, at process No. 2, to evaporate 250 CC of water with sulphuric acid, dissolve the ignited residue in 250 CC of distilled water, and take 50 CC for analysis.

† If 20 CC of baryta solution have been added, the excess of soap solution, to form a lather, will be greater; 2·8 degrees must be deducted. But it is perhaps better always to add 50 CC (100 degrees) of baryta. The deduction is then 4 degrees, and the loss of hardness on 100 degrees is the amount of alkali.

sulphate of baryta, gives the number of degrees of sulphuric acid.

7. Iron is determined in the usual manner by the permanganate of potash solution. 500 CC of the water are evaporated to a small bulk with sulphuric acid; the iron is reduced by zinc, and estimated by the permanganate of potash solution. Ten cubic centimeters are counted as one degree of  $\text{Fe}_2\text{O}_3$ .

If Silica be present, it will remain on redissolving the ignited sulphates, and if 250 CC of the water have been evaporated with sulphuric acid, it may be estimated by weighing.

In process 2, the oxide of iron becomes insoluble, and increases the amount of carbonic acid gas, from which it must be deducted.

All the processes here described are of very easy execution. The method of estimating carbonic gas is unequalled in exactness and facility of execution by any method I know, and the process for estimating the total capacity of saturation of the alkalies is extremely exact and satisfactory. The estimation of sulphuric acid, devised by M.M. Boutron and Boudet, is likewise of great precision.

I append examples of the calculation of an analysis performed by this process, to show the advantage obtained by the method of graduation I propose, in establishing an empirical formula for the salts contained in waters.

# 1. Analysis of the Water supplied by the Chatham Water Company to Fort Pitt.

1. Hardness .....	53°·7	<div> <div>Carbonic acid gas*</div> <div>Calcium</div> <div>Magnesium</div> <div>Iron</div> </div>
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\* The iron is to be deducted from the gross carbonic acid, 4 degrees.

2. Hardness after ignition with sulphuric acid	} 49°·7	{ Calcium Magnesium
3. Calcium ascertained by permanganate	} 48°·3	Calcium
4. Hardness after ignition with sulphuric acid, and 60 degrees of baryta added	} 53°·6	(Sodium loss 6°·4)
5. Chlorine .....	5°·5	
6. No sulphuric acid .....		
7. Iron .....	0°·2	

Deduction of an Empirical Formula for the Salts contained in the above Water. This calculation, so tedious by the ordinary method, becomes here of extreme simplicity. I combine the 5·5 degrees of chlorine with an equal number of degrees of sodium, a balance of ·9 degrees of sodium is left. This with the calcium and magnesium is calculated as carbonate.

	Deg.	Equiv.	Gm. per litre.	Grns. per gallon.
Carbonate of lime ...	48·3	× 50	= ·2415	× 70 = 16·905
Carbonate of magnesia	1·4	× 42	= ·0058	× 70 = ·406
Carbonate of soda ...	·9	× 53	= ·0047	× 70 = ·329
Chloride of sodium	5·5	× 58·5	= ·0321	× 70 = 2·247
Oxide of iron .....	·2	× 80	= ·0016	× 70 = ·112
Silica .....			= ·0020	× 70 = ·140
			·2877	20·132
Carbonic acid gas ...	3·8	× 44	× ·0167 =	= 2·52
		(2CO <sup>2</sup> )	8·93 CC	[cub. in. per gal.
Residue on ignition .....			·2810	= 19·680

## 2. Water from a Pump at Fort Pitt.

	Degrees.
Total hardness .....	36.8
Calcium and magnesium .....	21.0
Calcium .....	16.9
Sodium .....	5.0
Iron ( $\text{Fe}^2\text{O}^3$ ) .....	1.2
Sulphuric acid .....	4.8
Chlorine .....	3.6

	Deg.	Equiv.	Gm. per litre.	Grns. per gallon.
Carbonate of lime ...	16.9	$\times 50$	$= .0845$	$\times 70 = 5.915$
Carbonate of magnesia	7	$\times 42$	$= .0029$	$\times 70 = .203$
Carbonate of iron ...	1.2	$\times 116$		
		$2(\text{FeO}, \text{CO}^2)$	$= .0139$	$\times 70 = .973$
Sulphate of magnesia	3.4	$\times 60$	$= .0204$	$\times 70 = 1.428$
Sulphate of soda ...	1.4	$\times 71$	$= .0099$	$\times 70 = .693$
Chloride of sodium...	3.6	$\times 58.5$	$= .0210$	$\times 70 = 1.470$
			$.1526$	$10.682$
Carbonic acid gas ...	14.6	$\times 44$	$= .0642$	$= 31.3 \text{ CC pr. lit.}$
			$(\times .537)$	$(31.3 \text{ CC} \times 4.54$
Solids by evaporation .1500 per litre.				$\times .061 = 8.67$
				cub. in. per gal.)

I may mention that the solution of permanganate of potash, of the standard here employed, answers admirably for the estimation of organic matter in water. 500 CC of water are heated to  $70^\circ \text{C}$ . ( $156^\circ \text{Fahr.}$ ) with a few drops of pure sulphuric acid, and the standard solution is added, 1 CC at a time, until a colour, lasting for ten minutes, is obtained. Every 10 CC of test-solution thus decolorised is equal to one degree of organic matter, requiring one equivalent of oxygen for complete oxidation (corresponding to  $\text{C}^2\text{O}^3, \text{HO}$ , for example).

A few words as to the best manner of attaining the rapidity which forms one merit of this process. 250 CC of the water are first set to evaporate with a few drops of sulphuric acid for processes 2 and 4 ; the lime is also precipitated in 50 CC for process 3. By the time the total hardness is taken, and the chlorine, sulphuric acid, and iron estimated, the evaporation is finished and the residue ready to be taken in hand. Two or three analyses can thus be easily performed in a day. One point must be carefully observed : that the distilled water contain no carbonic acid gas. The delicacy of the soap-test for this gas is so great that the distilled water will speedily acquire one or two degrees of hardness, if left exposed to the air. If it has acquired any hardness from this cause, it should be boiled previously to use.

With reference to the determination of the sulphuric acid and alkalies by means of the soap solution, I can fully endorse the statements of Nicholson respecting their accuracy.

For instance, two solutions were made with pure sulphates of potash and soda, each containing 48 grains per gallon. On determining the strength by nitrate of baryta and soap solution, the yield in the case of sulphate of potash was in the proportion of 47·89 grains, and of soda 48·3 grains per gallon.

The estimation of sulphuric acid was of course involved in the same process, and therefore equally accurate.

The determination of the lime, and by difference the magnesia, has not yielded me such satisfactory results ; that is to say, the degree of hardness found by soap solution does not accurately accord with the amount found by experiment ; where the fault is I have had no time to decide.

The following is the analysis very carefully made by the ordinary gravimetric method, of a sample of water from an artesian well in Norwich. The well is now in process of boring, and has already reached over 1200 feet without arriving at the greensand. The water here examined is supposed to flow, not from that

depth, but from the great Norfolk chalk water-bearing fissure at between 3 and 400 feet.

Carbonate of lime .....	14·80	grains per gallon.
Carbonate of magnesia ...	1·72	"
Sulphate of lime .....	4·89	"
Chloride of sodium .....	4·52	"
Silica .....	0·19	"
Organic matter .....	1·16	"
Oxide of iron and alumina,	traces only	
<hr/>		
Total solid matter	27·28	"
Solid residue on evaporation	27·40	"

The results obtained with the same water by the volumetric plan were as follows :—

	Degrees.
Total hardness .....	59·0
Lime and magnesia .....	57·5
Lime .....	56·0
Sodium .....	12·0
Chlorine .....	11·5
Sulphuric acid .....	12·0

Calculated as under :—

	Deg.	Equiv.	Gm. per litre.	Grns. per gallon.
Carbonate of lime ...	44·0	× 50	= ·2200	× 70 = 15·400
Carbonate of magnesia	1·5	× 42	= ·0063	× 70 = 0·441
Sulphate of lime ...	11·5	× 68	= ·0782	× 70 = 5·470
Chloride of sodium...	11·5	× 58·5	= ·0672	× 70 = 4·910
Sulphate of soda ...	0·5	× 71	= ·0035	× 70 = 0·245
Silica determined in previous analysis				0·190
Organic matter	"	"		1·160
				<hr/>
				27·816
Total solid residue on evaporation				<hr/> 27·400



It will be seen that the magnesia is shown to be diminished by two-thirds of its quantity, as found by actual experiment, while the carbonate and sulphate of lime are increased by about the same weight each, as the magnesia has lost. Nevertheless, the general coincidence of the two results are extremely satisfactory; but I ought to say, that I failed to obtain such satisfaction in another case. I am, willing, however, to believe that this may have arisen from want of time to give the experiment the attention it required.

I am convinced, moreover, that the process requires exceedingly careful manipulation, to yield reliable results, such as can only be given by well-practised operators. The small quantities of water taken for examination and the delicate graduation of the burette, requiring not only extreme care in standardizing the test fluids and measuring the soap solution, but also in avoiding any traces of acid or other hardening substances in the vessels used during the processes of titration.

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#### ANALYSIS OF PHARMACEUTICAL SUBSTANCES AND PREPARATIONS.

§ 86. THE readiness and ease with which the volumetric system of determination may be applied, renders it especially useful for ascertaining the purity of the substances used in pharmacy, and also the strength of some of the preparations ordered in the pharmacopœia.

The following list is given as an indication of the extent to which the system may be applied; the numbers refer to the various sections contained in the foregoing part of the book.

The only apparatus and materials required for the bulk of

the substances are 1 burette, Fig. 1, 1 ditto, Fig. 6, 2 or 3 pipettes, Fig. 7, 3 graduated flasks, a few beakers and porcelain dishes, also funnels, filters, and glass rods. A good ordinary balance, carrying about 300 grains and turning with  $\frac{1}{10}$ th or  $\frac{1}{20}$ th of a grain, will be sufficiently exact if somewhat large quantities be weighed, and afterward subdivided in solution by the measuring flasks and pipettes.

If the operator desires to prepare his own standard solutions, additional apparatus is needed. Carefully prepared solutions may, however, be purchased at a trifling cost, for particulars of which see a list at the end of the book.

	§	§		§	§
Acetum destillat. ....	29		Ferri carbon. ....	47, 22a	
Acid. acetic. fort. ....	29		„ „ sacch. ...	47, 22a	
„ „ glac. ....	29		„ ammon. citr. ...	47	
„ arsenious ....	64		„ iodid. ....	67	
„ citric ....	33		„ „ syrup. ....	67	
„ hydrocyanic. dil. ....	77		„ sesquichl. tinct. ....	47	
„ hydrochloric ...	24		„ ammon. chlor. ....	47	
„ nitric. ....	25		Ferrum reductum ....	47	
„ sulphuric ....	27		Hydrarg. am. chlor. ...	62	
„ phosphoric ....	78		„ bichlor. ....	62	
„ tartaric. ....	33		„ chlorid. ....	62	
Aq. lauro cerasi. ....	77		„ biniodid. ...	62, 67	
„ amygd. amar. ...	77		Hydrarg. oxyd. rubrum	62	
Ammon. carbon. ....	16, 22		Iodinium ....	67, 45	
Antim. pot. tart. ....	66		„ tinct. co. ...	67, 45	
„ pulv. co. ....	66		„ „ sx. ...	67, 45	
Argenti nitras ....	76		Liquor ammon. ....	16	
Calcis permanganas ...	43		„ „ acet. ....	16	
Ferri oxydum. ....	47		„ arsenic. chlor. ..	64	
„ sulphas. ....	47		„ arsenicalis. ....	64	

	§	§		§	§
Liquor calcis .....	19,	60	Potassæ chloras. ....	68,	75
„ „ chlorinat. ....	70		„ nitras .....	26,	41
„ plumbi acet. ...	61		„ permanganas..	43	
„ potassæ .....	14		Potassii iodid. ....	67	
„ sodæ chlorinat. ....	70		„ sulphuret. ...	54	
Magnes. carbon. ....	22,	32	Sodæ carbon. ....	13	
„ calcin. ....	32		„ bicarb. ....	13	
Potassæ hydras .....	14		„ phosph. ....	78	
„ bicarb. ....	14		Spt. ammon. arom. ...	16	
„ bitart. ....	33		Zinci carbon. ....	22	
„ carbon. ....	14		„ oxydum .....	32,	53

## Weights and Measures.

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480·0 grains Troy	=	1 oz. Troy.
437·5 „	=	1 oz. Avoirdupois.
7000·0 „	=	1 lb. Avoirdupois.
5760·0 „	=	1 lb. Troy.

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The imperial gallon contains of distilled water at 62° Fahr. (16·5 C) .....	70,000 grains.
The pint ( $\frac{1}{8}$ of gallon) .....	8,750 „
The fluid ounce ( $\frac{1}{16}$ of pint) .....	437·5 „

The pint equals 34·66 cubic inches.

MEASURES OF WEIGHT.					
	In English Grains.	In Troy Ounces =480 Grains.	In Avoirdupois Lbs.=7,000 Grains.	In Cwts.=112 Lbs. =784,000 Grains.	Tons=20 Cwts. =1680,000 Grains.
Milligramme .....	0.015432	0.000032	0.00000922	0.00000002	0.000000001
Centigramme .....	0.154323	0.000322	0.0000220	0.00000020	0.000000010
Decigramme .....	1.543235	0.003215	0.0002205	0.00000197	0.000000098
Gramme .....	15.432349	0.032151	0.0022046	0.00001968	0.000000984
Decagramme .....	154.323488	0.321507	0.0220462	0.00019684	0.000009842
Hectogramme .....	1543.234880	3.215073	0.2204621	0.00196841	0.000098421
Kilogramme .....	15432.348800	32.150727	2.2046213	0.01968412	0.000984206
Myriogramme .....	154323.488000	321.507267	22.0462126	0.19684118	0.009842059
1 Grain=0.064798950 Gramme. - 1 Troy oz.=31.103496 Gram. 1 lb. Avd.=0.45359265 Kilogr. 1 Cwt.=50.80237689 Kilogr.					
MEASURES OF CAPACITY.					
	In Cubic Inches.	In Cubic Feet =1,728 Cubic Inches.	In Pints =34.65923 Cubic Inches.	In Gallons= 8 Pints=277.27884 Cubic Inches.	In Bushels=8 Gal- lons=2218.19075 Cubic Inches.
Millilitre, or cubic centimètre ...	0.061027	0.0000353	0.001761	0.00022010	0.000027512
Centilitre, or 10 cubic centimètres	0.610271	0.0003532	0.017608	0.00220097	0.000275121
Decilitre, or 100 cubic centimètres	6.102705	0.0035317	0.176077	0.02200967	0.002751208
Litre, or cubic décimètre .....	61.027052	0.0353166	1.760773	0.22009668	0.027512085
Decalitre, or centistère .....	610.270515	0.3531658	17.607734	2.20096677	0.275120846
Hectolitre, or decistère .....	6102.705152	3.5316581	176.077341	22.00966767	2.751208459
Kilolitre, or stère, or cubic mètre	61027.051519	35.3165807	1760.773414	220.09667675	27.512084594
Myriolitre, or decastère .....	610270.515194	353.1658074	17607.734140	2200.96676750	275.120845937
1 Cubic Inch=16.3861759 Cubic Centimètres. 1 Cubic Foot=28.3153119 Cubic Decimètres. 1 Gallon=4.54347989 Litres.					



**ACCURATELY GRADUATED INSTRUMENTS AND TITRATED  
SOLUTIONS.**

In order to suit the convenience of medical men, pharmaceutical chemists, manufacturers, and others, who may not possess accurate and expensive balances and other necessary apparatus, or who may not have time to prepare their own standard solutions, the undersigned have made arrangements for supplying accurately titrated solutions such as are used in Mr. Sutton's laboratory, and also very carefully graduated instruments for the use of the same.

All instruments are made under Mr. Sutton's direction, engraved with his name, and carefully tested by him before being sent out. The standard solutions are prepared by himself only.

The prices attached to the various articles, are as reasonable as is consistent with the utmost care in their manufacture and verification, and are calculated upon such a rate of profit as to exclude all risks of credit.

It is requested, therefore, that all orders be accompanied with a remittance by cheque or post-order, including 10 per cent. extra for bottles and packing in Great Britain, and 15 per cent. for all foreign orders.

HARPER AND SUTTON,

OPERATIVE CHEMISTS,

NORWICH.

**Apparatus.**

Mohr's Burette, with elastic tube and clip, Fig. 1,  
graduated to 110 CC or dm. each division=1 CC

or dm. ....	6/6
Ditto, 110 CC or dm. in $\frac{1}{2}$ ..	7/6
Ditto, 60     "     " $\frac{1}{2}$ ..	6/6
Ditto, 60     "     " $\frac{1}{3}$ ..	7/6
Ditto, 30     "     " $\frac{1}{3}$ ..	5/6
Ditto, 30     "     " $\frac{1}{10}$ ..	6/6

Gay Lussac's Burette, with tube and foot, Fig. 4, same prices.

Burette with inner tube and elastic ball and foot, each, extra	1/
Graduated Pipettes, 100 CC or dm. in $\frac{1}{2}$ .....	6/
"    "    50    "    " $\frac{1}{2}$ .....	4/
"    "    50    "    " $\frac{1}{3}$ .....	6/
"    "    50    "    " $\frac{1}{10}$ .....	7/6
"    "    20    "    " $\frac{1}{10}$ .....	5/
"    "    10    "    " $\frac{1}{10}$ .....	4/
Whole Pipettes, delivering to a mark, 100 .....	3/6
"                "                50 .....	3/
"                "                20 .....	3/
"                "                1, 2, 5, 10 .....	2/6
Measuring Flasks, stoppered, 1 litre or 1000 dm. ....	4/6
"                "                500 CC or dm. ....	3/6
"                "                300    "    .....	3/
"                "                100, 200, and 250 CC or dm. ....	2/6
Erdmann's Floats .....	each 2/
Stoppered Test Mixer, 1 litre or 1000 dm. in 100 div. ...	10/
Wooden Supports for 1 Mohr's Burette .....	3/6
"    "    2    "    "    .....	4/6
"    "    6    "    "    .....	10/
Delicate Balance, in glass case, to carry 400 grains, with set of grain or gramme weights, £5 10s.	

**Pure Titrated Solutions, packed in stoppered bottles.**

	Per Imp. Pint.	Per 4-Gal.
Normal Sulphuric, Nitric, or Oxalic Acids, § 11 ...	2/	6/
"    Carbonate of Soda, § 11 .....	2/	6/
"    Caustic Potash or Soda, § 11 .....	2/6	7/6
"    Ammonio Sulphate of Copper, § 30 .....	2/6	7/6
"    Chloride of Barium, § 28 .....	2/	6/
Decinormal Permanganate of Potash, from pure crystals, § 43 .....	2/6	7/6

## TITRATED SOLUTIONS.

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	Per Imp. Pint.	Per 4-Gal.
Decinormal Bichromate of ditto, § 44 .....	2/	6/
„ Iodine Solution, § 45 .....	2/6	7/6
„ Hyposulphite of Soda, § 45 .....	2/	6/
„ Arsenite of Soda, § 46 .....	2/	6/
„ Nitrate of Silver, § 74 .....	3/6	12/
„ Chloride of Sodium, § 74 .....	2/	6/
Empirical Nitrate of Silver, for Photographic Solutions, § 76, 1 .....	3/6	12/
Ditto, ditto, Chloride of Sodium, § 76, 1 .....	2/	5/
Standard Iodide of Starch Solution, § 76, 2 .....	2/6	7/6
„ Solution of Salt for Assaying Silver, § 76, 3 .....	1/	3/6
Decimal ditto, ditto .....	1/	3/6
„ Solution of Silver, ditto .....	2/6	7/6
Standard Nitrate or Acetate of Uranium, for Phos- phoric and Arsenic Acids, § 78, 1 .....	3/	10/
Standard Phosphate of Soda, ditto .....	2/	6/
Decinormal Nitrate of Lead, for Phosphoric Acid, § 82, 2 .....	2/	6/
Ditto, Phosphate of Soda .....	2/	6/
Standard Copper Solution for Sugar, § 79 & 80, 10 .....	3/6	12/
„ Nitrate of Mercury for Urea, § 80, 3 .....	3/6	12/
„ „ for Chlorides, § 80, 2 .....	2/6	7/6
„ Ferrocyanide of Potassium for Albumen, § 80, 11 b .....	2/	6/
„ Soap Solution for the Hardness of Water, by Clark's method .....	2/6	7/6
„ Water, ditto, § 84 .....	1/6	5/
„ Soap Solution for the Analysis of Water, § 85 .....	3/6	12/
„ Solution of Lime for ditto .....	2/	6/
„ Baryta Solutions for ditto .....	each 2/	6/
„ Nitrate of Silver for ditto .....	2/6	8/
„ Oxalate of Ammonia for ditto .....	1/6	5/
„ Permanganate of Potash .....	1/6	5/



## Chemicals prepared specially for Standard Solutions, &amp;c.

	Per lb.	Per oz.
Pure Double Sulphate of Iron and Ammonia ...	6/	/6
„ Bichromate of Potash .....	5/	/6
„ Oxalic Acid .....	5/	/6
„ Permanganate of Potash .....	40/	3/6
„ Nitrate of Silver .....		8/
„ Nitrate of Uranium .....		4/
„ Acetate of ditto .....		4/
„ Hyposulphite of Soda .....	5/	/6
„ Ferrocyanide of Potassium .....	5/	/6
„ Ferridcyanide of ditto .....	8/	/8
„ Chloride Barium .....	5/	/6
„ Chloride Sodium .....	5/	/6
„ Iodine .....		3/6
„ Iodide of Potassium .....		3/6
„ Precipitated Carbonate of Lime .....	5/	/6
„ Phosphate of Soda .....	5/	/6
„ Oxide of Mercury .....	10/	1/
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